Title
Development of Chemical Processes for the Recycling of Carbon Fiber/Epoxy Composites

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Publication Date
2020

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA

Los Angeles

Development of Chemical Processes for the Recycling of Carbon Fiber/Epoxy Composites

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Douglas Chen

2020

ABSTRACT OF THE DISSERTATION

Development of Chemical Processes

for the Recycling of Carbon Fiber/Epoxy Composites

by

Douglas Chen

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2020

Professor Jenn-Ming Yang, Chair

Carbon fiber/epoxy composites are a vital and heavily used component in a variety of industries, ranging from aerospace to sports. However, major difficulties may soon arise in regard to environmental considerations for their disposal. These composites are designed to be strong and resilient, and thus are difficult to break down or decompose. The only current option for carbon fiber/epoxy composite wastes is to leave them in landfills or plane graveyards. The high price of carbon fiber also makes finding ways to recover and reuse carbon fiber very attractive. The purpose of this dissertation is to investigate an inexpensive method to break down the epoxy in carbon fiber/epoxy composites and recover fibers while maintaining their mechanical strength.

A new chemical solvolysis process was utilized to oxidize and decompose the epoxy in carbon fiber-reinforced epoxy composites, allowing for carbon fiber recovery and recycling. This

process involved heating the composite in a mixture of ethanol and hydrogen peroxide at elevated temperatures for 4 hours. This process results in significant epoxy removal with minimal fiber strength loss. Epoxy removal was confirmed with visual and mass analysis, scanning electron microscopy and electron dispersive spectroscopy, and thermogravimetric analysis. The liquid byproduct solution remaining was chemically analyzed using gas chromatography/mass spectroscopy and found to contain organic compounds that could be attributed to the degradation of epoxy by the solution.

A kinetic model was developed for the purpose of identifying optimal parameters for the reaction. Parameters considered included time, temperature, concentrations of the reactants, and the amount of surface area exposed to the oxidizing solution. Mass loss over time was studied for each reaction variable while keeping the other parameters static, creating a mass loss rate that could be plotted against each parameter. The fittings for these plots were used to identify the constants to be used in the model. The model was compared to experimental data and found to correlate well, with an average error below 8%.

The new chemical solvolysis process in this study was compared to using 98% pure sulfuric acid to dissolve the epoxy. The solvolysis process was found to remove epoxy at a higher rate, while keeping similar fiber strength when comparing samples processed for similar fiber recovery performance. These comparisons resulted in the conclusion that the solvolysis process performs better than dissolution by sulfuric acid.

A further modification to the solvolysis process involves the same mixture of ethanol and hydrogen peroxide with the addition of ferrous ions in an acidic environment. This process could potentially be done at lower temperatures and lower concentrations of hydrogen peroxide, and thus could allow for a reduction in costs when recovering fibers using this process. Initial

experiments did confirm the ability to remove significant amounts of epoxy at much lower temperatures and lower concentrations of hydrogen peroxide.

The dissertation of Douglas Chen is approved.

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University of California, Los Angeles

2020

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Acknowledgements

This work would not have been possible without the continuous time and support from my advisor, Professor Jenn-Ming Yang. I would also like to thank the committee members, Professors Ximin He, Xiaochun Li, and Qibing Pei, for taking the time to evaluate and approve my work. I would also like to acknowledge and give special thanks to Greg Khitrov for assistance with GCMS, and Igor De Rosa for assistance with tensile testing and TGA.

I would also like to thank my parents for giving me support in my times of need, as well as my friends for helping maintain my sanity throughout this process.

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Chapter 1 Introduction and Motivation

Introduction

Carbon fiber-reinforced polymer (CFRP) has become an important structural material now widespread throughout many industries. Its combination of high strength and light weight results in considerable use in a wide variety of applications, ranging from aerospace to athletic equipment. With such heavy use, the end-of-life stage must now be considered. As of now, there is no simple environmentally friendly disposal method for CFRP. A wide variety of methods are currently being researched to find a way to reuse the materials in CFRP, whether it be the carbon fiber itself, the epoxy, or both.

Carbon Fiber Composites Overview

Carbon fibers are fibers composed of primarily graphitic carbon. They have a high tensile strength starting at 1000 MPa up to 7000 MPa, while having the relatively low density of carbon[1]. With this combination of properties, one can construct products and devices that are both very strong and lightweight. Initial carbon fibers were first produced by carbonizing cotton and rayon at high temperatures, but these early fibers were comprised of only 30% carbon for fibers produced from rayon. Commercial fibers with good mechanical properties were not mass-produced until polyacrylonitrile was used as a precursor, which increased the carbon content to 50%. Further developments in processing conditions raised the carbon content to above 85%[2].

The morphology and properties of carbon fibers vary depending on the precursor and processing conditions used. The primary atomic structure is composed of graphene sheets ordered so that it is graphitic, turbostratic, or more typically a combination of the two[3]. The graphitic

structure has the sheets stacked parallel to each other in an ordered, crystalline pattern. In the turbostratic structure the sheets tend to be stacked erratically, and can split, fold, or tilt out of plane.

Carbon fibers are especially useful when incorporated in composite materials. The most prevalent form is carbon fiber in an epoxy matrix. The epoxy enables the material to maintain a low weight as well as a high stiffness, while the fibers within contribute a high tensile strength. Thus, carbon fiber/epoxy composites have mechanical strength as high as metals such as titanium alloys and steels yet are much lower in density[3]. These superior qualities make them good materials for use in applications where the product must be both strong and lightweight. Specifically, beneficial applications include its use in aerospace, automotive, and sports equipment.

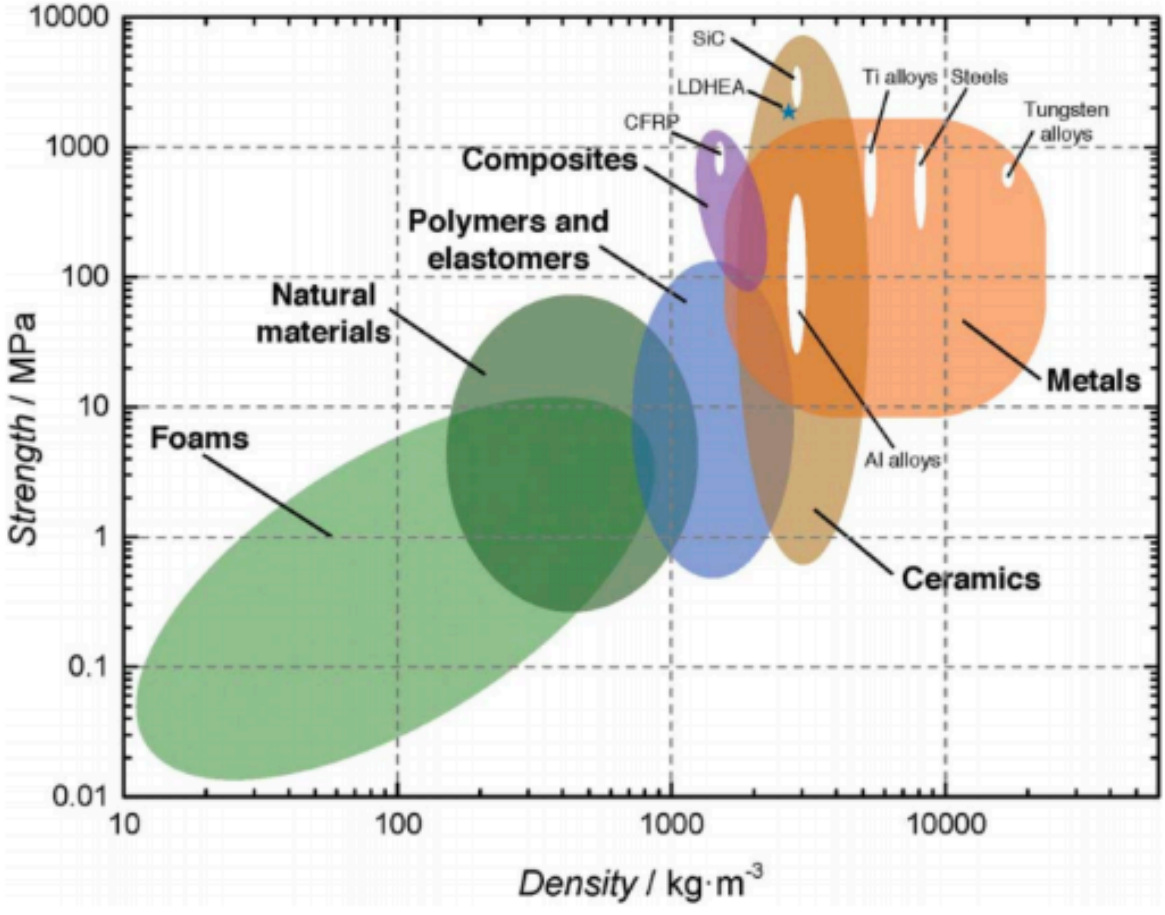

Fig. 1-1 Tensile strength vs density for variety of materials[4]

Airplane manufacturers Boeing and Airbus are implementing carbon fiber composites in their latest planes, the 787, the 777x, and the A350 XWB. Carbon fiber is also being used more extensively in wind turbine blades to allow for larger blades. It is seeing more use in high end car bodies, notably the BMW i3 and m3 as well as race cars. Sports equipment such as baseball bats and tennis rackets also see more utilization of carbon fiber composites.

Carbon Fiber/Epoxy Composite Manufacturing and Properties

Carbon fiber is available in a few different forms, depending on the precursor used. The predominant type of fiber used is polyacrylonitrile (PAN) carbon fiber due to its relative ease of production while maintaining better mechanical properties. Production of this type involves first synthesizing a polyacrylonitrile precursor by polymerizing acrylonitrile with initiators, either in solution or suspension. Precursor fibers are then spun out of the PAN solution.

These precursor fibers are oxidized and stabilized at temperatures above 200°C[3]. The nitrile groups in PAN result in a high melting point, allowing the polymer to degrade to form cyclic carbon chains before melting. During this step cyclization occurs and graphitic planes begin to form. This reaction is exothermic, and thus conditions must be controlled. If the system is heated too quickly the yield of carbon will be reduced and defects will form in the fibers. The inclusion of additional chemical compounds such as carboxylic acid and acrylamide improved the rate at the which fibers could be stabilized so that the process could be completed faster. The inclusion of some oxygen in the process was also found to improve cyclization and crosslinking, improving the

carbon yield and mechanical properties[5]. Sulfur dioxide, hydrochloric acid, and bromine was also found to have the same effect[6,7].

Many different mechanisms and models have been suggested for the cyclization process, seen in figure 1-2. The most commonly cited is the cyclic dehydrated structure in figure 1-2 (a), developed by Houtz[8]. Schurz et al proposed an azomethine crosslinking figure 1-2 (b)[9]. Standage and Matkowski suggested including oxygen due to the lack of oxygen in the previous models, as seen in figure 2 (c)[10]. The models shown in figures 1-2 (g) and 1-2 (h) account for possible unreacted nitrile groups that could remain[11, 12].

After stabilization and oxidation, the fibers are treated at temperatures greater than 1000°C in inert gas such as nitrogen to carbonize the polymer. In this step most non-carbon atoms are removed, and the polymer undergoes further crosslinking. The fibers undergo dehydration and denitrogenation. The dehydration develops the cyclic polymer into graphitic ribbons, while the denitrogenation grow the ribbons into sheets as seen in figure 1-3. Thus, graphene planes begin to form and orient along the fiber axis. It is believed that lightly stretching the fibers to induce slight tension during this process ultimately improves the mechanical properties. Strength of the fibers increase with carbonization temperature up to 1500°C, beyond which the modulus increases at the cost of decreased tensile strength[5]. It was also found that applying a magnetic field parallel to the fiber axis reduced surface defects and improved tensile strength by 14%[13]. Similar to oxidation and stabilization, a carbonization rate that is too fast will result in increased defects. However, a rate that is too slow will remove too much nitrogen, of which some is needed for high strength fibers. The use of microwave-generated plasma has been found to reduce the time required for carbonization by 2/3[14,15].

An optional final step of 3000°C in inert gas can then be applied to cause graphitization, which increases the modulus due to the growth of the graphitic crystalline regions, increased orientation along the fiber axis, and reduced voids within the fiber[3]. However, more defects are formed, reducing the tensile strength. At these temperatures an argon gas must be used, as nitrogen gas would react with the carbon. The inclusion of boron in the gas flow could cause the fiber to absorb boron into the graphitic planes, which could improve crystallization as well as shear stress[16].

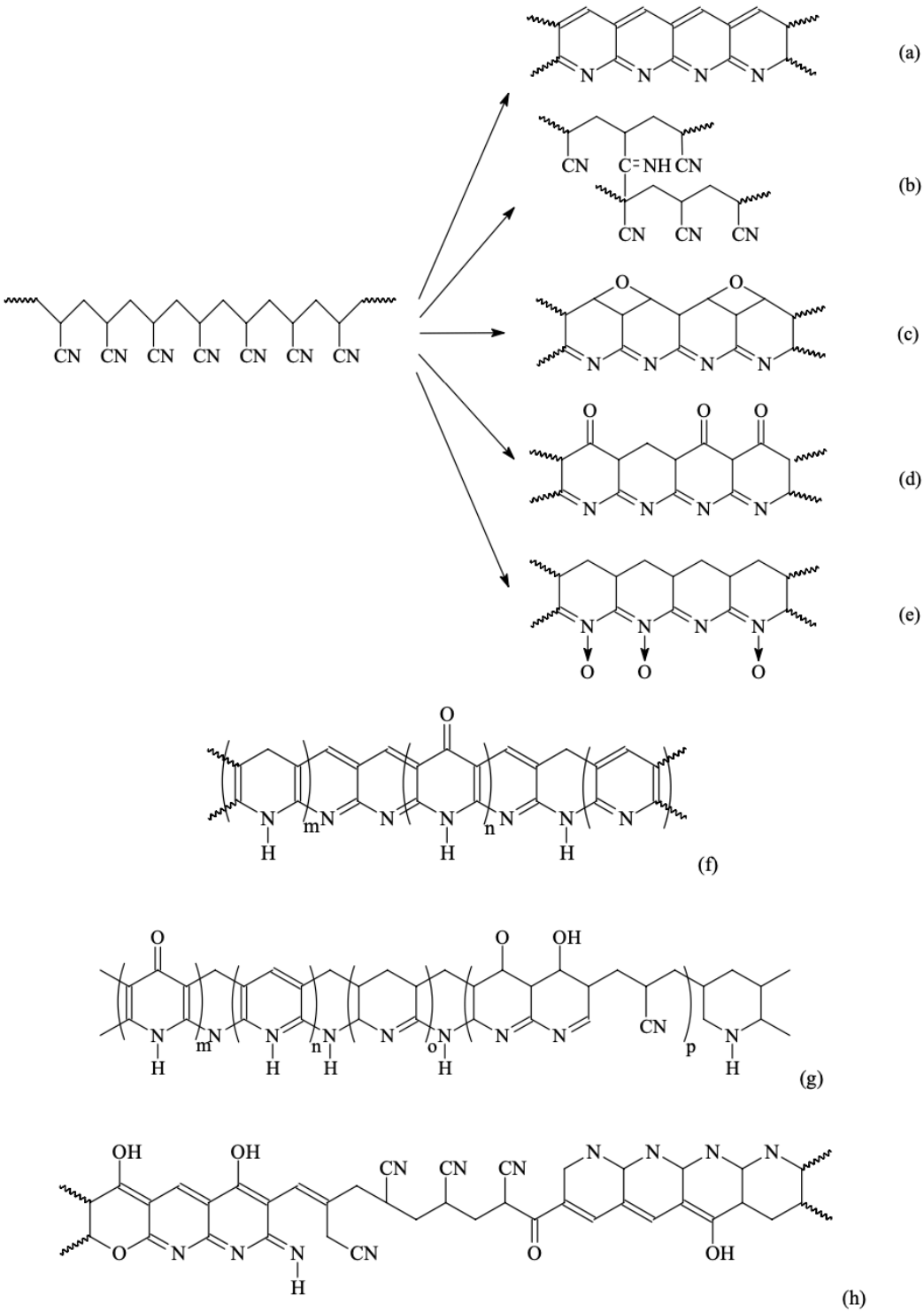

Fig. 1-2 Possible results from the stabilization and oxidation of PAN[3]

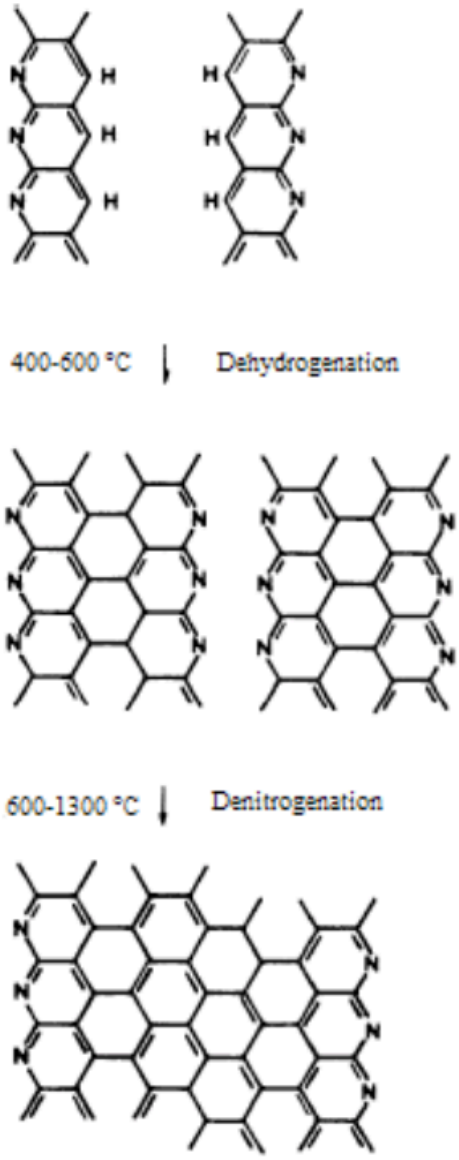

Fig. 1-3 Formation of graphite by dehydrogenation and denitrogenation[12]

Pitch-based carbon fibers are produced by spinning precursor fibers from a viscoelastic polymer pitch derived from petroleum, tar, or plants[3]. Similar to the production of PAN-based fibers, pitch-based fibers are then stabilized in air at 200°C – 400°C and carbonized at 800°C – 1200°C or graphitized at around 2800°C. Depending on the polymer used, the fibers can be either isotropic or anisotropic. For isotropic fibers the pitch used must be homogeneous and fluid. Anisotropic mesophase pitch-based fiber production initially had problems due to the formation of mesophase spheres. This formation was later prevented by including new processes such as fractionation, hydrogen gas purge, and adding hydrogen-donating compounds to the pitch. Mesophase-pitch-based fibers have a higher tensile strength and tensile modulus than those of isotropic-pitch-based fibers.

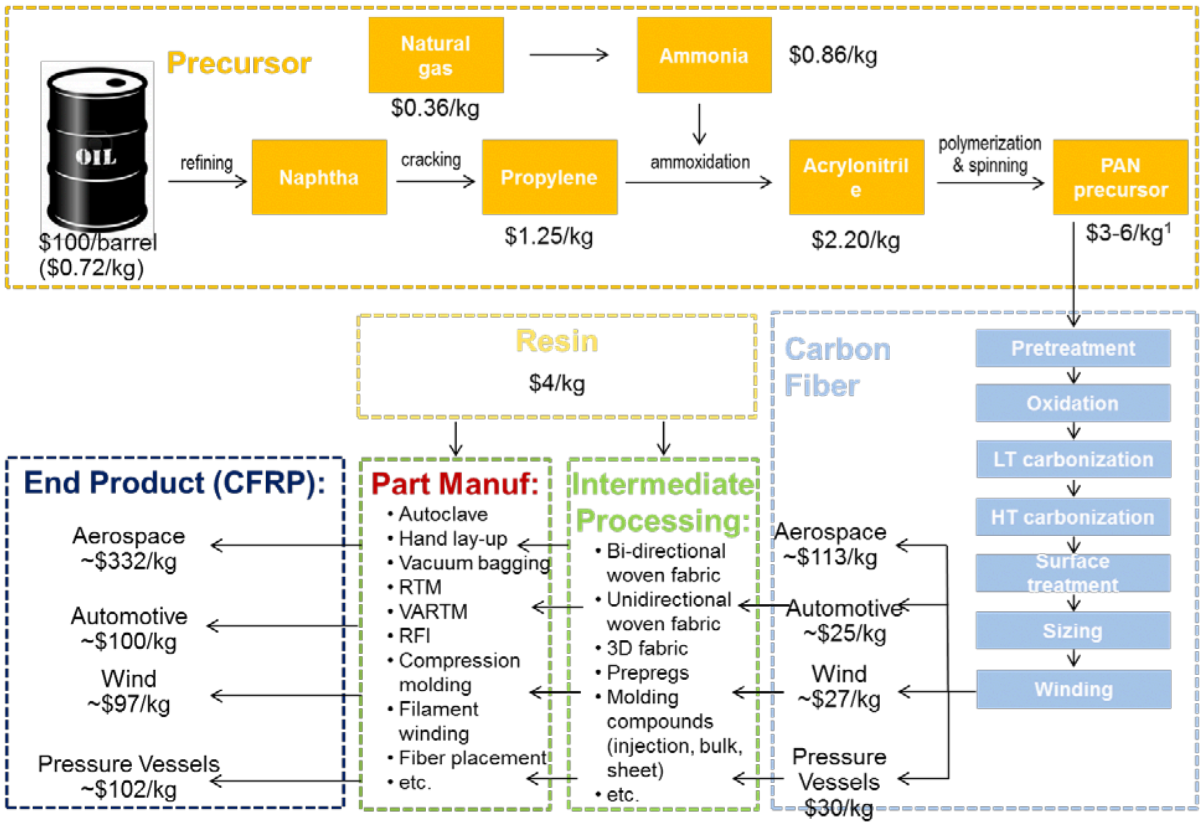

Fig. 1-4 Flowchart illustrating production process of carbon fiber from synthesis to final epoxy composite product[17]

Vapor-grown carbon fibers utilize metal particle catalysts as seeds for growth[3]. A hydrocarbon gas is fed over catalysts either seeded on a substrate or floating in the reactor space. Growth using a floating catalyst results in a higher yield of fibers produced. Depending on specific operating conditions, vapor-grown fibers can have the highest tensile strength while maintaining high tensile modulus. However, this process is complex and thus prohibitively expensive for industrial use.

High-strength fibers with ordered graphitic structures can be created by using mesophase pitch or vapor growth[3]. While PAN-based fibers generally result in turbostratic fibers, though some regions of the fiber may become graphitic through the optional graphitization step. Perret

and Ruland reported a wrinkled ribbon model with voids oriented in the fiber direction, as shown in figure 1-4[4].

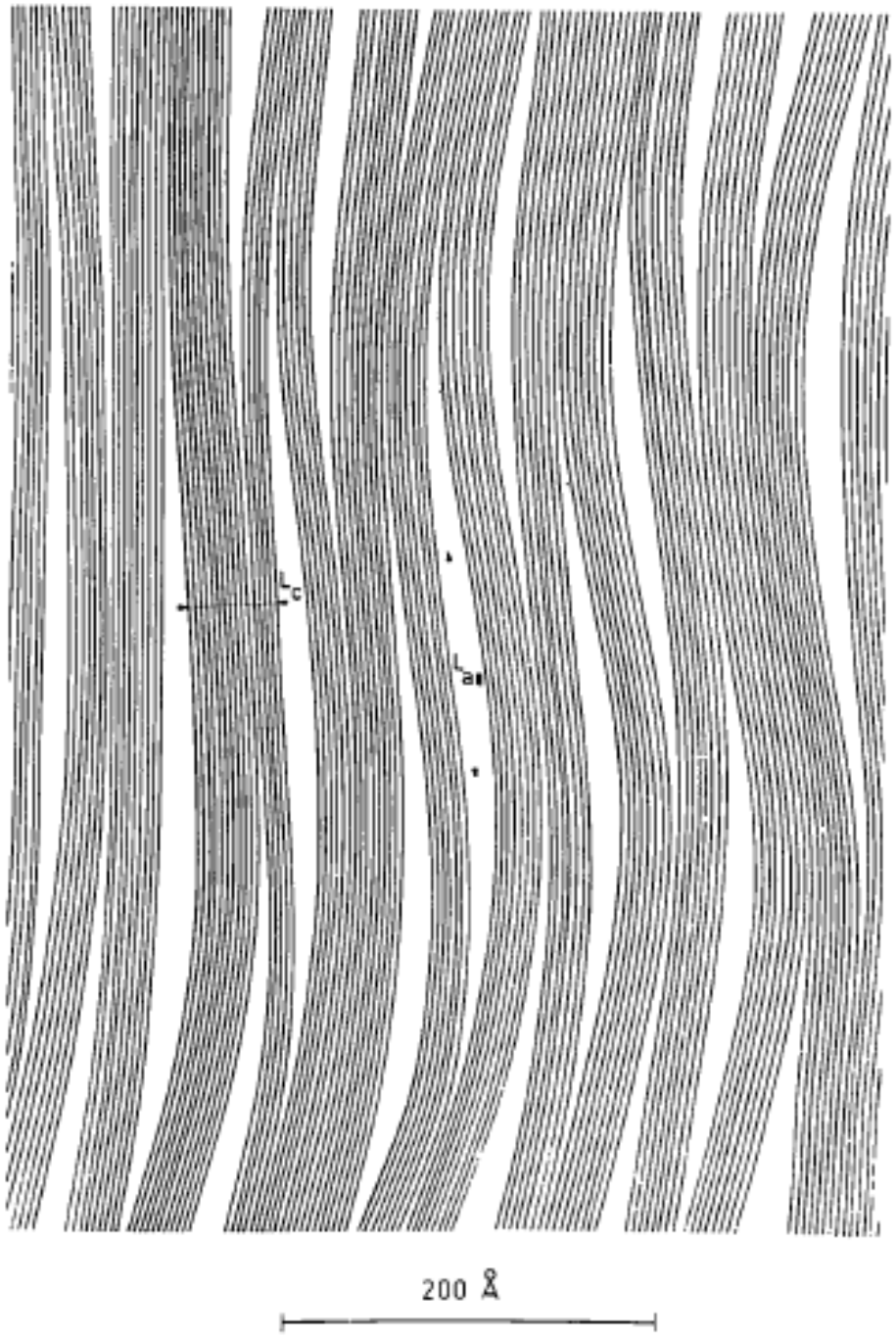

Fig. 1-5 Reported lateral microstructure of PAN-based carbon fibers[18]

Carbon fibers that are more graphitic in structure will have a higher Young's modulus. This high crystallinity can be achieved by growth via mesophase pitch-spinning or vapor growth. It should however be noted that the increase in crystalline regions also cause higher stress concentrations at the grain boundaries, and also make the fibers more sensitive to defects. In comparison the turbostratic fibers fabricated from PAN have higher tensile strength.

Carbon fiber composites are created by impregnating layers of fibers with epoxy and curing the assembly. Typically, the epoxy is only partially cured and the composite is stored in a freezer as a prepreg to prevent further curing. When creating a composite part, the prepreg is removed from the freezer and shaped along a mold. This part is then cured at elevated temperatures, usually either in a vacuum bag or under pressure. The fully cured composite is then removed from the mold and finalized.

Orientation of the fibers in the composite greatly affects the mechanical properties, as the tensile strength and modulus of the fibers is effective only along the direction of the fiber. In order to maximize the strength of components along all directions, multiple layers of carbon fiber must be placed in different orientations. These orientations usually include 0°, 90°, and 45° angles to each other.

Environmental Challenges

Several challenges arise when considering the end-of-life of carbon fiber composite products, specifically due to how resilient the thermosetting epoxies are designed to be. These thermoset epoxies are cured at temperatures above 125°C to form a significantly high density of covalent crosslinking bonds. As a result of these newly formed chemical bonds, these epoxies are

thermally and mechanically strong as well as chemically inert. While the resiliency of these composites makes them very useful in a wide variety of products, it makes their end-of-life considerations problematic. When carbon fiber/epoxy composite products are no longer useable, they currently become nondegradable/nonrecyclable landfill. Thus, a major challenge presents itself when considering the environmental effects of carbon fiber/epoxy composites when they are finished.

Another consideration is whether carbon fiber can be recovered from these composites and reused. The high temperatures and pressures required to synthesize carbon fiber results in high costs for the material. If recycled carbon fiber can be introduced into the market at reduced costs, consumer-grade carbon fiber products could become cheaper and thus more widely available.

Chapter 2 Literature Survey on Existing Methods for Recycling of Carbon/Epxoy Composites

Introduction

Current research on recycling carbon fiber composites can be categorized into three broad subjects, which are mechanical, thermal, and chemical. Mechanical methods physically break apart the composites to create filler for other composites. Thermal and chemical methods decompose the epoxy matrix allowing in order to recover clean carbon fiber that can be reused. Thermal methods decompose the epoxy matrix by heating them in air, inert gas, or a specialized packed bed reactor. Chemical methods use solvolysis to decompose the epoxy matrix instead of heat.

Mechanical Recycling

Regarding the mechanical process, CFRP is crushed or shredded into small pieces[19,20,21]. The pieces can then be used as either filler or reinforcement, recycled products are then separated by size, resulting in powders composed of epoxy as well as carbon fibers of varying lengths still embedded in epoxy resin. These powders can be used as fillers. However, they are not economically competitive with standard fillers such as calcium carbonate or silica, which are much cheaper. The recovered fiber portions can be incorporated as reinforcement in new composite products. However, the mechanical properties of these new composites are compromised due to poor bonding between the resin and recycled products. If fibers of longer length could be recovered it would be preferable, as more of the advantages of continuous carbon fiber would be available. Both possible products make mechanical grinding a simple and inexpensive process.

Unfortunately, the process seems to be economically unfeasible as the value of the end products would most likely be unable to match the costs of breaking CFRP into pieces and grinding them into powders and small fiber pieces.

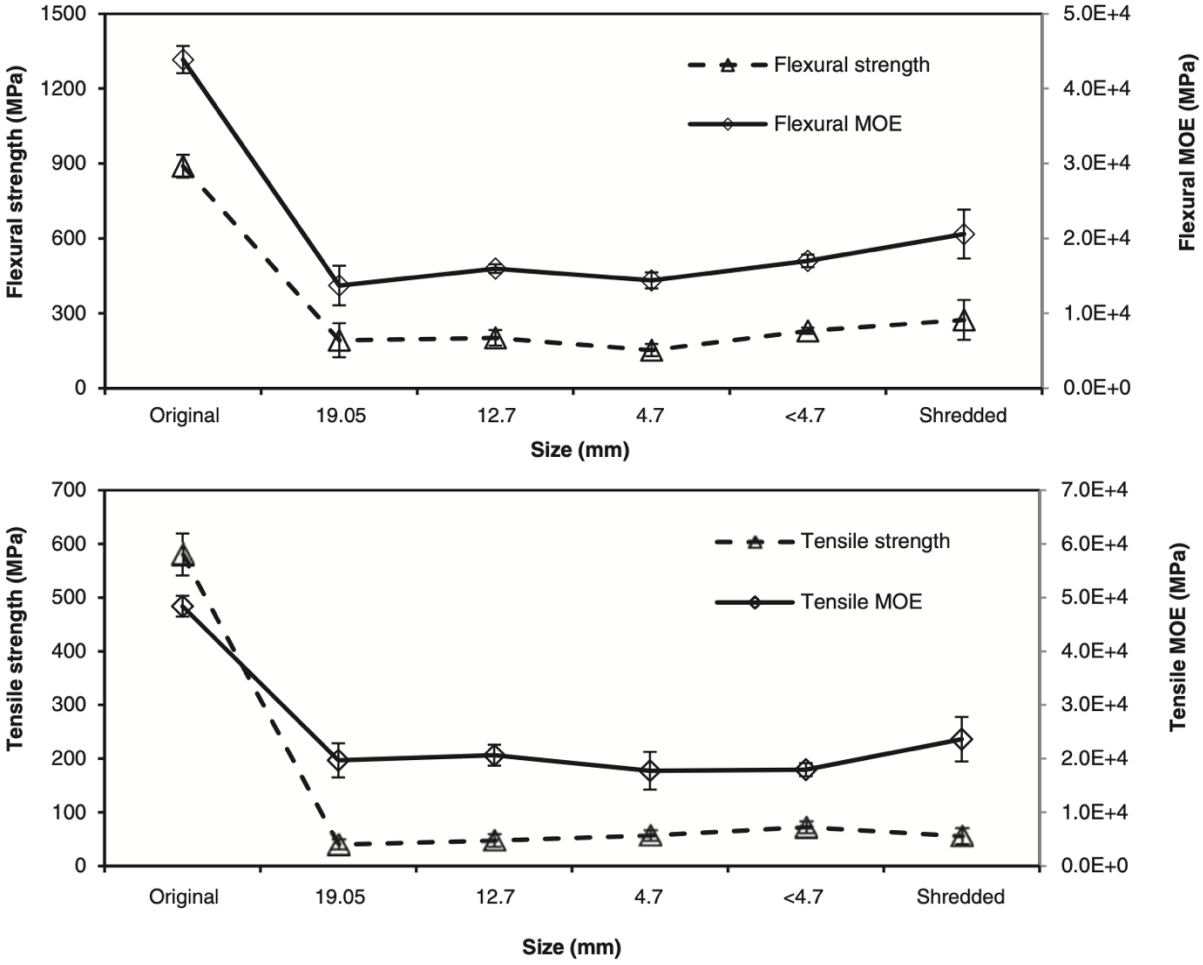

Fig. 2-1 Strength comparison between original CFRP and composites incorporated mechanically milled/ground recyclate[43]

Thermal Processes

In terms of thermal processes, CFRP can be incinerated for energy generation or recycled via pyrolysis, fluidized bed pyrolysis, or microwave-assisted pyrolysis[20,21,23,24]. Incineration will ultimately produce electricity but will also produce ash to be sent to landfill and will provide no material that can be reused. In standard pyrolysis, CFRP is heated between 450°C and 700°C, depending on what resin is used. These high temperatures decompose the epoxy, releasing the carbon fibers from the composite. These pyrolysis procedures performed typically result in a char that requires further heat treatment to remove. This long exposure to high temperatures can also result in degraded fiber, especially if the fiber is vulnerable to oxidation. Char residue can be reduced and fiber strength can be improved by controlling the atmospheric conditions of the oven. These conditions typically involve nitrogen or superheated steam.

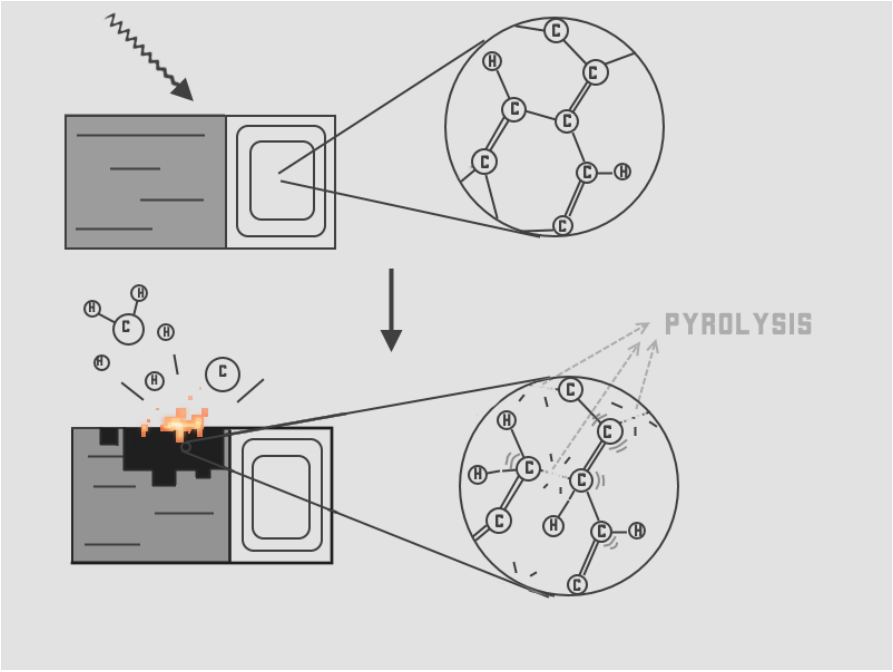

Fig. 2-2 Diagram demonstrating pyrolosis decomposition

Fluidized Bed

Groups such as Yip et al. used the fluidized bed process to recycle composite material[25]. This process typically utilizes a stream of hot air or gas flowing through a bed of particles such as silica sand so that the particulates mix with the air and the combination behave as a fluid. The underlying mechanism is the same as pyrolysis, as the material is again heated to degrade the resin so that the fibers can be recovered. Temperatures of 550°C result in complete reclamation of fibers that could potentially be rebounded to a resin matrix but have a strength degradation of 25%. However, the high temperatures and complicated process flow would require sophisticated equipment, making such a process industrially expensive.

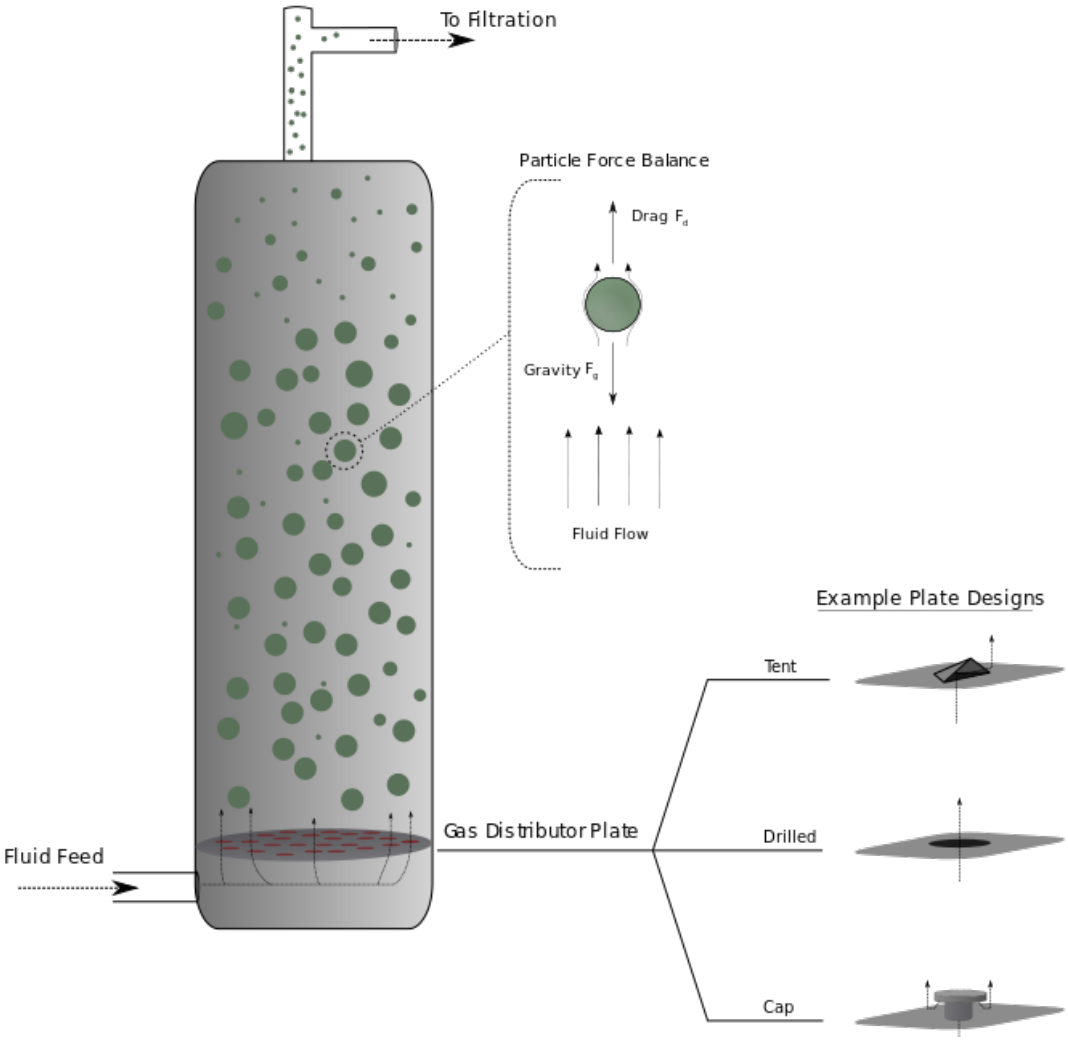

Fig. 2-3 Illustration of fluidized bed reactor

Microwave-Assisted Pyrolysis

Microwave-assisted pyrolysis uses microwave radiation for faster heating due to more direct energy transfer, but again sees significant fiber degradation unless controlling atmospheric conditions. An argon flow atmosphere resulted in the removal of all resin with only 0.7% strength lost[26]. Pyrolysis methods thus can provide reusable carbon fibers but due to the use of very high temperatures could be expensive in energy and capital costs, especially in the use of specialized and sophisticated equipment for controlled atmospheres, fluidized beds and microwave-assisted pyrolysis.

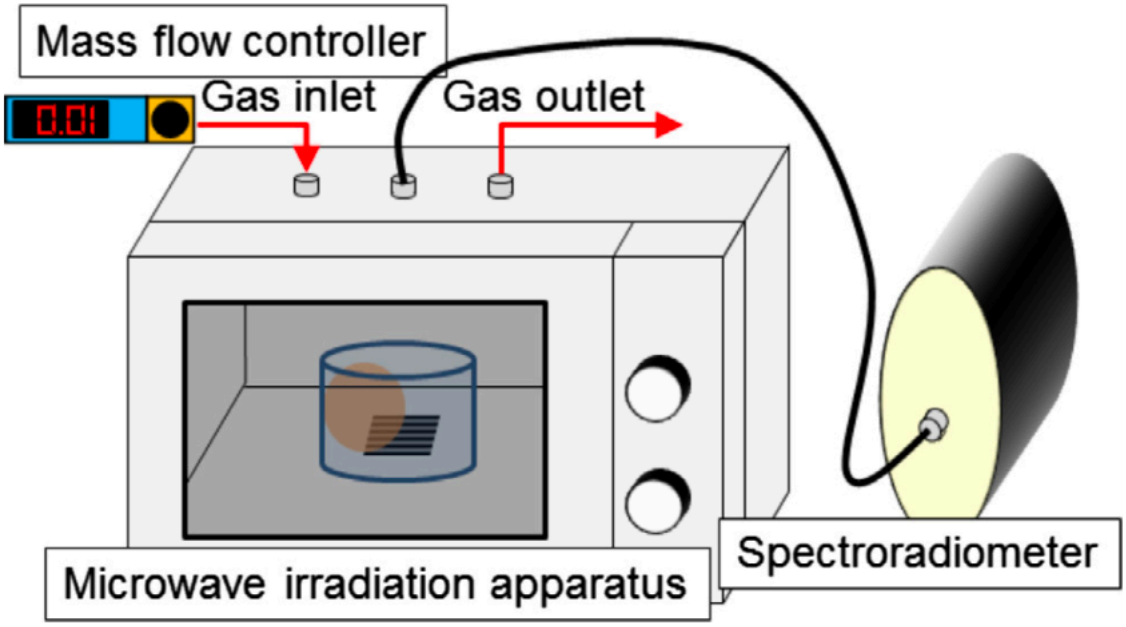

Fig. 2-4 Experimental setup for microwave-assisted pyrolysis[26]

Supercritical Processes

Attempts are also being made to recycle CFRP via chemical solvolysis, wherein a chemical solution is used to decompose the resin. Solvolysis research can be categorized into either high or low temperature processes. High temperature involves using supercritical fluids, mostly consisting of alcohols or water[21,24]. The solution is heated and pressurized past its critical point, resulting in a system that has the dissolution properties of a liquid and the effusive properties of a gas.

Hernanz et al. investigated the use of supercritical water to decompose the epoxy[27]. Supercritical water required operating conditions of above 10 MPa and 300°C and removed upwards of 48 wt. % epoxy. They noted the maximum percentage removed was 79.3 wt. % at 28 MPa and 400°C, though with an alkali catalyst added 95.4 wt. % could be achieved. However, these operating conditions would be difficult and expensive to maintain in industrial operations.

Research into supercritical alcohols investigates a variety of solvents. Piñero-Hernanz, García-Serna et al. found the use of methanol, ethanol, 1-propanol, and acetone at 250°C – 400°C with an alkali catalyst could decompose 95% of the resin in 15 minutes, with 85% – 99% of the fiber strength retained[28]. Okajima et al. found supercritical methanol reduced tensile strength by 9%[29]. They also found that acetone performed best at amine-cured epoxy removal when compared to methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butanol, and methyl ethyl ketone. In contrast, Cheng et al. found n-butanol to result in the most resin removal while retaining 98% of the original tensile strength[30]. Overall the amount of fibers recovered and retained strength of the fibers are very good. However, the use of high temperatures above 250°C while pressurizing reactors to 8 MPa and higher would require the use of sophisticated equipment capable of maintaining such extreme conditions. Such equipment and energy usage would make these processes costly, and ultimately economically unfeasible.

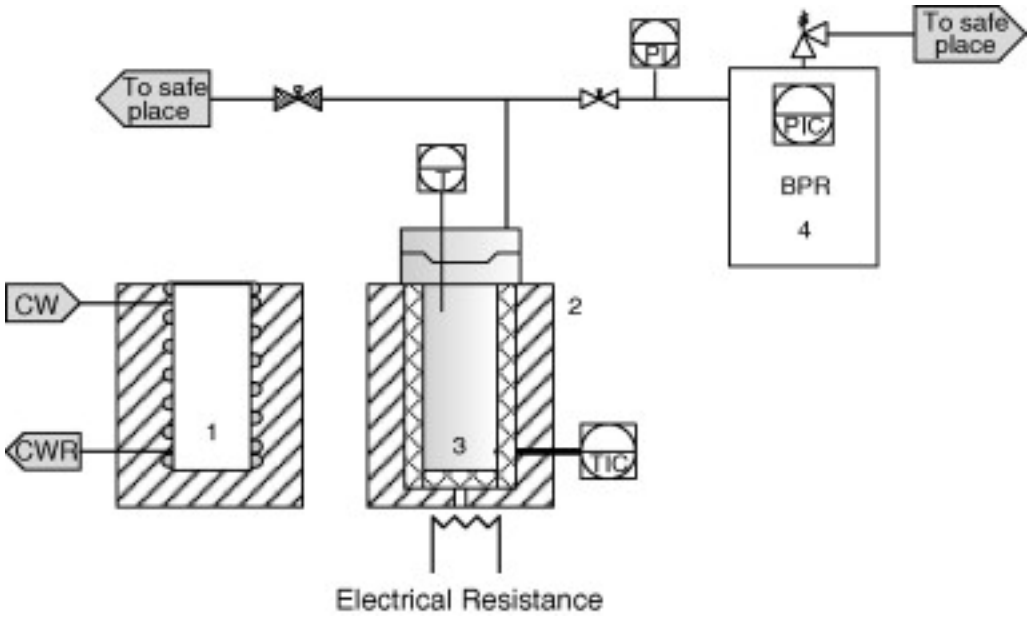

Fig. 2-5 Flow Diagram demonstrating setup required for supercritical reactor[31]

Novel Chemical Methods

Lower temperature solvolysis has typically involved either acidic or catalytic conditions, though other novel methods have also been investigated. Sun et al. used CFRP as an anode with a stainless-steel plate cathode and a 3% NaCl solution as an electrolyte in an electrochemical syste[32]. After passing a voltage of 2.6 V across the electrodes for 21 days the recovered fibers retained similar strength to virgin fibers. However, the time required for this process would be nonideal in industrial applications. Das and Varughese used dilute nitric acid and H_2O_2 in an ultrasonic system at 60°C to decompose 95% of the epoxy and found that use of ultrasonic tripled the decomposition ratio compared when compared to the same solution without ultrasonic[33].

Acidic Decomposition

Liu et al. used nitric acid to decompose epoxy, finding complete fiber recovery after 12 hours at 90°C[34]. Strength loss was measured to be 1.1%. These results were found to be improved when compared to results from the use of sulfuric or hydrochloric acid. Although the resulting fiber recovery rate and fiber strength retention are very high, the required amount of time and safety considerations could potentially make the process of using concentrated sulfuric acid unfeasible.

Hydrogen Peroxide Solutions

Outside of the use of unconventional methods and acid is the application of hydrogen peroxide mixed in various solutions. Of particular note are the experiments performed by Li et al. where hydrogen peroxide solution (30% in water) was reacted with acetone in an autoclave chamber to decompose cured samples[35]. CFRP samples were expanded using acetic acid then placed in solution at elevated temperatures. The hydrogen peroxide thermally decomposed to form hydroxyl radicals, a powerful oxidizer that reacts with both the acetone as well as the epoxy resin. The acetone is believed to have aided in dissolving the resin. It was found that 90% of the epoxy was successfully dissolved, and the fibers retained most of their strength. However, a side-product developed with this reaction is triacetone triperoxide, which is an organic explosive. Due to the major safety hazards from this reaction, an alternative to acetone could lead to a safe, cheap alternative to decompose the resin and recover fibers.

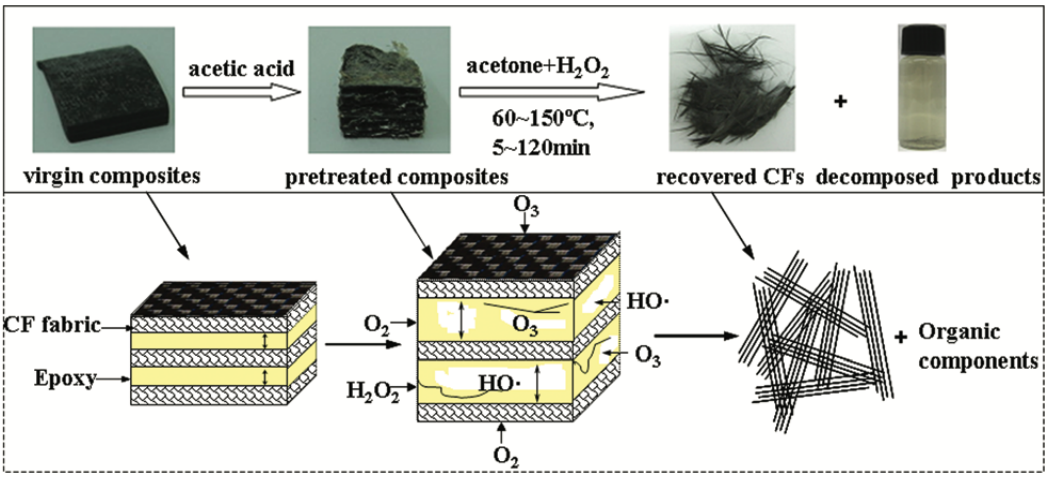

Fig. 2-6 Flow Diagram for composite decomposition in hydrogen peroxide solution[35]

Xu et al. used N,N-dimethylformamide in a 1:1 volumetric ratio for successful removal of epoxy with a 5% tensile strength decrease[36]. However N,N-dimethylformamide is a known toxic substance, and use of it in CFRP recycling may prove to be a significant safety hazard. Since the primary mechanism of this reaction is the decomposition of hydrogen peroxide to form hydroxyl radicals, an alternative chemical solvent to acetone or N,N-dimethylformamide would be ideal.

Decomposition of organic materials by hydrogen peroxide is a heavily researched topic. The use of hydrogen peroxide to decompose bisphenol A (BPA) has been investigated, especially when using a process known as the Fenton reaction. In the Fenton reaction, a reagent or catalyst causes hydrogen peroxide to form the oxidizing hydroxyl radicals. A number of materials and methods are known to cause this reaction, including ferrous ions as well as photocatalysts such as TiO_2. This photocatalytic Fenton process in particular has been investigated as a way to treat BPA.

Many groups have used UV radiation and ferrous ions to react with hydrogen peroxide and form hydroxyl radicals. They found the system to be effective in breaking apart the molecule

and rupturing the aromatic ring, ultimately resulting in formic acid, acetic acid, and acetaldehyde[37,38]. The ferrous ions have also been found to form hydroxyl radicals from hydrogen peroxide, though without UV radiation or acidic conditions a solid iron (III) hydroxide precipitate forms. This precipitation results in the removal of the ferrous ion catalysts from the system. In order to prevent this the ferrous must be regenerated either through photolysis, an acidic environment with a pH level below 4.5, or a combination of the two. While the photocatalytic requirements may be limiting due to intensive energy requirements or severely limited operations, investigation into the standard Fenton method may be useful due to more efficient hydroxyl radical generation.

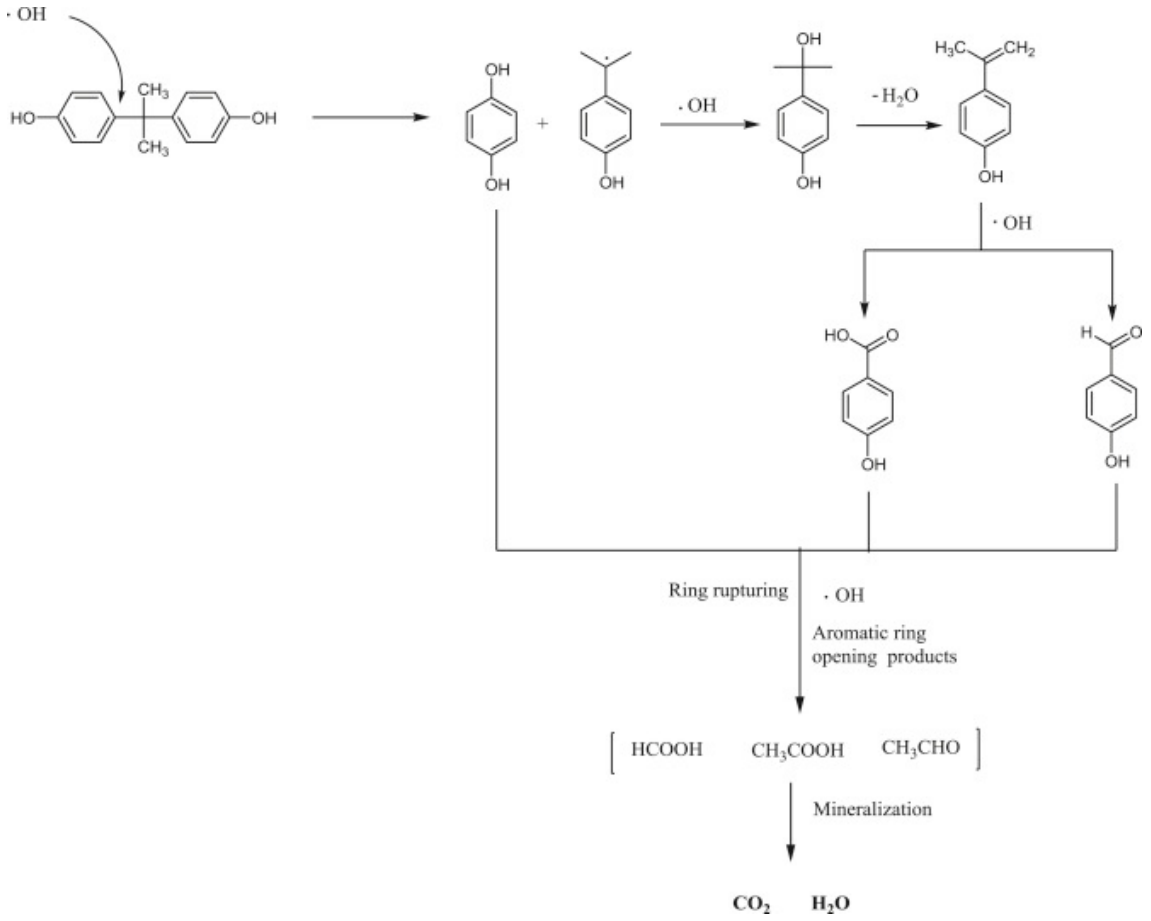

Fig. 2-7 Proposed mechanisms for the decomposition of BPA into small molecules due to hydroxyl radical attack[37]

Proposed Work

An ideal recycling system for carbon fiber composites would require low temperature and pressure, requiring low cost materials and equipment. It would have a minimal impact on the environment and would be safe to operate. With these desired conditions in consideration, oxidation by hydrogen peroxide appears to be a good process. However, an alternative process that substitutes another chemical for acetone or dimethylformamide is necessary. The work of this dissertation is to investigate a system combining ethanol and hydrogen peroxide and compare it to the methods currently being researched as well as the utilization of 99% pure sulfuric acid. Ethanol is considered as a substitute to acetone due to its behavior as a solvent and its safety. Ethanol is known to oxidize to acetaldehyde, which can then be further oxidized to acetic acid. Both compounds are relatively safe and non-toxic. Its behavior as an alcohol could also provide some synergy, since it is a widely used solvent and is also used in supercritical alcohol investigations.

The kinetics of the reaction between the hydrogen peroxide/ethanol solution and the epoxy is studied, with the effects of temperature, chemical concentrations, and exposed surface area on the rate of epoxy dissolution is investigated. The use of this solution is compared to the use of highly concentrated sulfuric acid, primarily in terms of carbon fiber recovery performance and tensile strength retention. This comparison will give some insight into the performance of the proposed ethanol/hydrogen peroxide system relative to other methods.

An ethanol/hydrogen peroxide system modified for the Fenton reaction is also analyzed. It includes ferric ions in a slightly acidic system. In both processes the hydrogen peroxide should form hydroxyl radicals that react with the ethanol to form radical byproducts that attack and decompose the epoxy, with ethanol additionally acting as a solvent. With the Fenton process, the hydroxyl radicals could be created faster and more efficiently, potentially resulting in a faster and

more efficient process that works at a lower temperature and with a lower concentration of hydrogen peroxide.

Chapter 3 Materials and Experimental Methods

Sample Preparation

This work proposes a chemical solvolysis method using a solution of ethanol combined with hydrogen peroxide, 30 wt% in water. The volumes of each chemical varied between 5 mL and 25 mL, with deionized water used in some cases to maintain a total volume of 30 mL. Temperatures ranging from 80°C to 150°C in intervals of 10°C were used. CFRP samples were prepared by curing PAN-based carbon fiber weaves embedded in a BPA-based epoxy comprised of Epon 828 and Epikure W, acting as the precursor and hardener respectively. Five layers were embedded in the epoxy resin mixture. This wet layup underwent a two-stage cure of 2 hours at 85°C then 2 hours at 150°C in vacuum. These cured boards were then cut into approximately 2.54 cm squares.

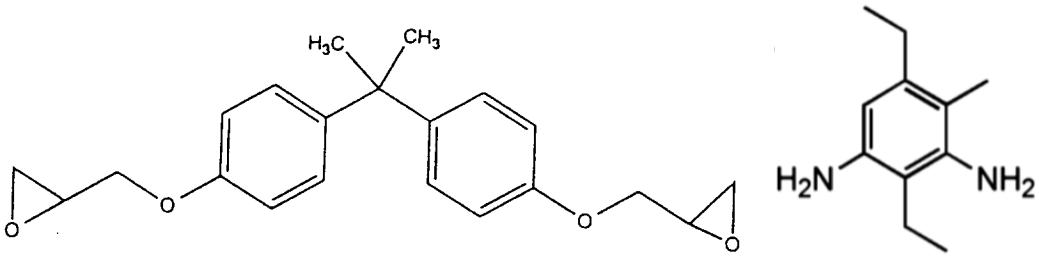

Fig. 3-1 Epon 828 epoxy resin (left) and Epikure W

Experimental Setups

Two experimental setups were initially used: a pressure vessel in an oven and a closed reflux apparatus warmed in an oil bath. The pressure vessel was a commercially available 500 mL Teflon vessel encased in a stainless-steel container, seen in figure 3-2. The reflux apparatus in figure 3-3 was a glass flask in a silicone oil bath heated by a hot plate attached to a glass reflux cylinder. Water was run through the reflux cylinder to cool and condense vapors from the heated solution. In the case of the pressure vessel the reaction was run for approximately 4 hours, while the reflux setup had to be run for more than 12 hours to achieve significant and observable results. Due to the significant difference in time, the reflux setup was disregarded in favor of the pressure vessel in oven. Experiments performed to develop the kinetic model were run at various times in order to determine rates at which mass was lost, as well as at varying temperatures and concentrations. Kinetic model parameters were determined by fitting experimental data to known kinetic model equations using Microsoft Excel, in particular using equations for the Arrhenius temperature relation as well as the power equations for chemical concentrations.

Fig. 3-2 Autoclave vessel and oven setup

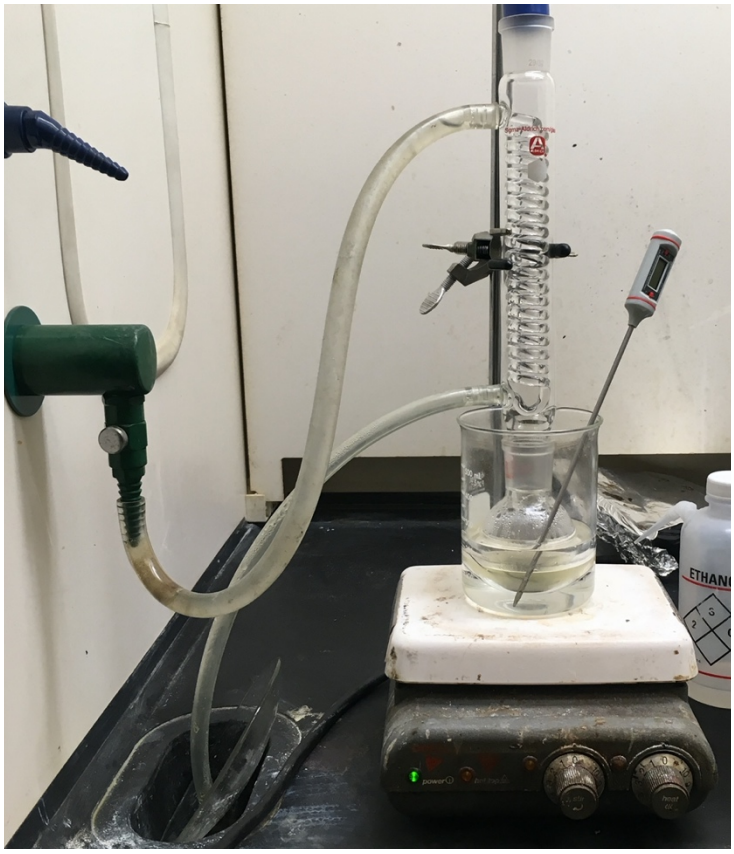

Fig. 3-3 Reflux Setup

Experiments performed followed three different categories: a mixture of hydrogen peroxide solution and ethanol, only sulfuric acid, and a mixture of hydrogen peroxide solution, ethanol, iron sulfate heptahydrate, and a small amount of sulfuric acid. The ethanol used included both 100% and denatured ethanol with no discernible difference in results. The hydrogen peroxide solution used was 30% by mass in water with stabilizer purchased from Sigma-Aldrich. Experiments using sulfuric acid utilized 98% pure sulfuric acid, heated to 120°C in the Teflon/stainless-steel pressure vessel in the oven. The results of these experiments were compared to CFRP samples processed in hydrogen peroxide/sulfuric acid in similar conditions. Experiments for the Fenton reaction

used the same chemicals as the previous experiments, with the addition of 8 mg iron sulfate heptahydrate dissolved in 1 mL deionized water. 0.5 mL sulfuric acid was added to keep a low pH level. Ethanol and sulfuric acid were acquired from the UCLA chemical store, and the hydrogen peroxide solution and iron sulfate heptahydrate were acquired from Sigma Aldrich.

Characterization Techniques

Samples of composites and carbon fibers were characterized using scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), Instron testing, and thermogravimetric analysis (TGA). SEM, EDS, and TGA were used to determine the efficiency of epoxy removal from the CFRP samples and recovered carbon fibers. SEM images were analyzed to visually determine whether epoxy was still present on the composite samples or fibers. EDS was used to chemically identify whether epoxy was still present. TGA was used to determine whether epoxy was still present due to the presence of any heterogeneous mass change. The Instron testing machine was used to test tensile strengths of fibers recovered from the hydrogen peroxide/ethanol system, the sulfuric acid system, and the Fenton reaction system. The chemical composition of the liquid byproduct solution was determined using gas chromatography/mass spectroscopy.

Methodology

The mass of each sample was measured before and after the experiments to determine how much mass was lost. A number of experiments were performed with all parameters kept constant except for time, which ranged between 1 and 4 hours. The changes in mass were plotted with corresponding time, and a linear equation was fit to determine the rate at which mass was lost. Rates were determined for multiple values of each parameter. Graphs were made to analyze the

relationship between rate of mass loss and each specific parameter. For each of the variables used in the kinetic model, and quantitative equations were fit to the plots in order to determine values of the constants present in the model. The same methodology was used to determine mass loss rates for the sulfuric acid and Fenton reaction systems.

Chapter 4 Effects of Using Hydrogen Peroxide and Ethanol on Epoxy Decomposition and Fiber Strength

Introduction

Hydrogen peroxide has three different dissociation pathways. It can behave as an acid and dissociate into a proton and hydroperoxyl anion. With the addition of a significant amount of energy or the use of a catalyst, the O-H or O-O bonds can be cleaved. This would result in a hydroperoxyl radical and hydrogen radical or two hydroxyl radicals. Under elevated temperatures, hydrogen peroxide will also decompose into water and oxygen. In the presence of organic compounds, the radicals can attack a variety of positions in the compounds. Due to this ability to readily decompose organic substances, oxidation by hydrogen peroxide has become an area of interest to treat organic wastes. The work presented here determines the efficacy of the hydrogen peroxide/ethanol solution in removal of epoxy and recovered carbon fiber retention strength retention.

Composite and Fiber Quality

Due to the favorable time conditions, only the results of the pressure vessel experiments were focused on. Visual inspection found significant changes, as epoxy was missing or colored dark brown and fibers were exposed and released. Masses of samples dissolved over various times were measure and changes in mass were plotted against time in figure 4-1. The results from this graph confirmed that mass was removed from the sample.

SEM images of samples processed for various times show epoxy being removed and are shown in figures 4-2, 4-3, and 4-4. In figure 4-2 a pristine and unprocessed sample of CFRP is

seen as carbon fibers buried in cured epoxy. In comparison, figure 4-3 shows a sample processed for 2 hours in hydrogen peroxide and ethanol. It can be seen that the epoxy is partially removed with fibers at the surface exposed. The epoxy remaining is cracked throughout, indicating expansion due to oxidation. After 4 hours fibers were released from the sample and could also be easily pulled from the sample. A collection of these fibers were analyzed in figure 4-4 and found to have no epoxy present.

Figures 4-5, 4-6, 4-7, and 4-8 are SEM images of fibers recovered from samples processed at various temperatures. The fibers appear to be the same in all images, indicating no change in the fibers with change in temperature. It could thus be determined that changes in process temperature does not appear to change the structure of the fibers.

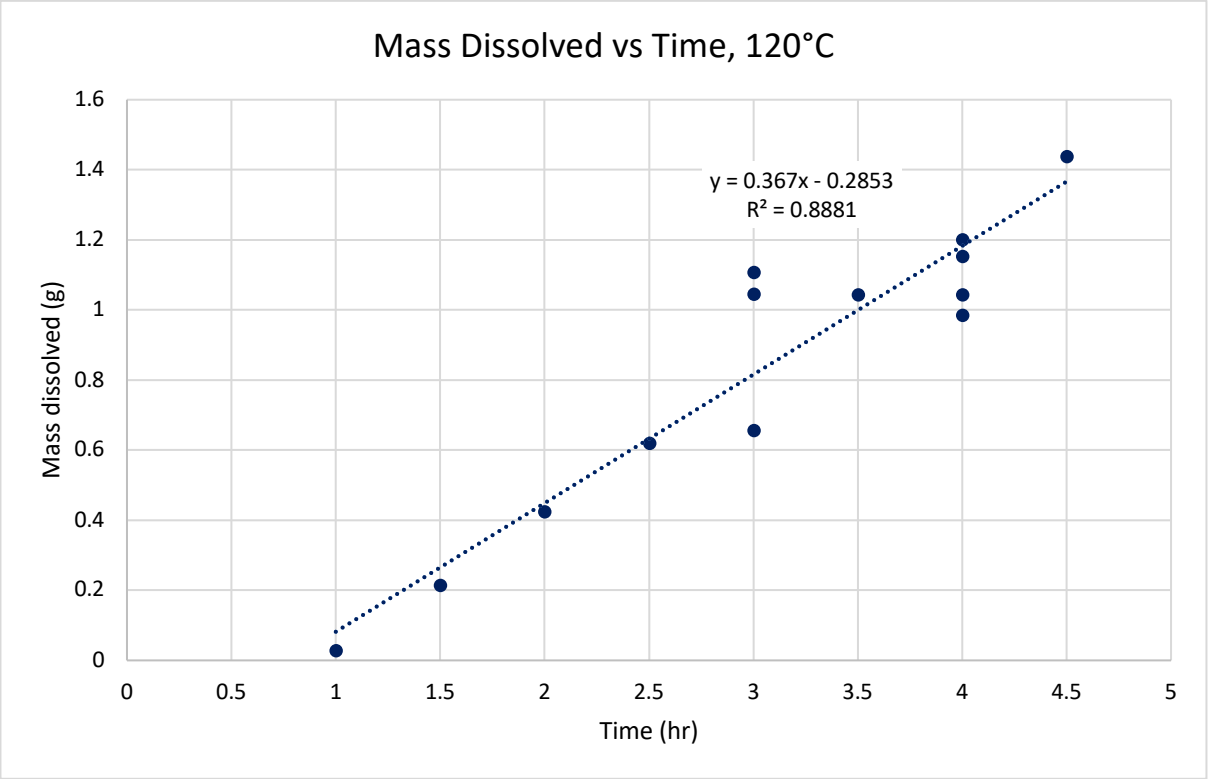

Fig. 4-1 Mass dissolved plotted against time, 120°C. Estimated 0.367 g dissolved per hour, with offset for heating to reaction temperature.

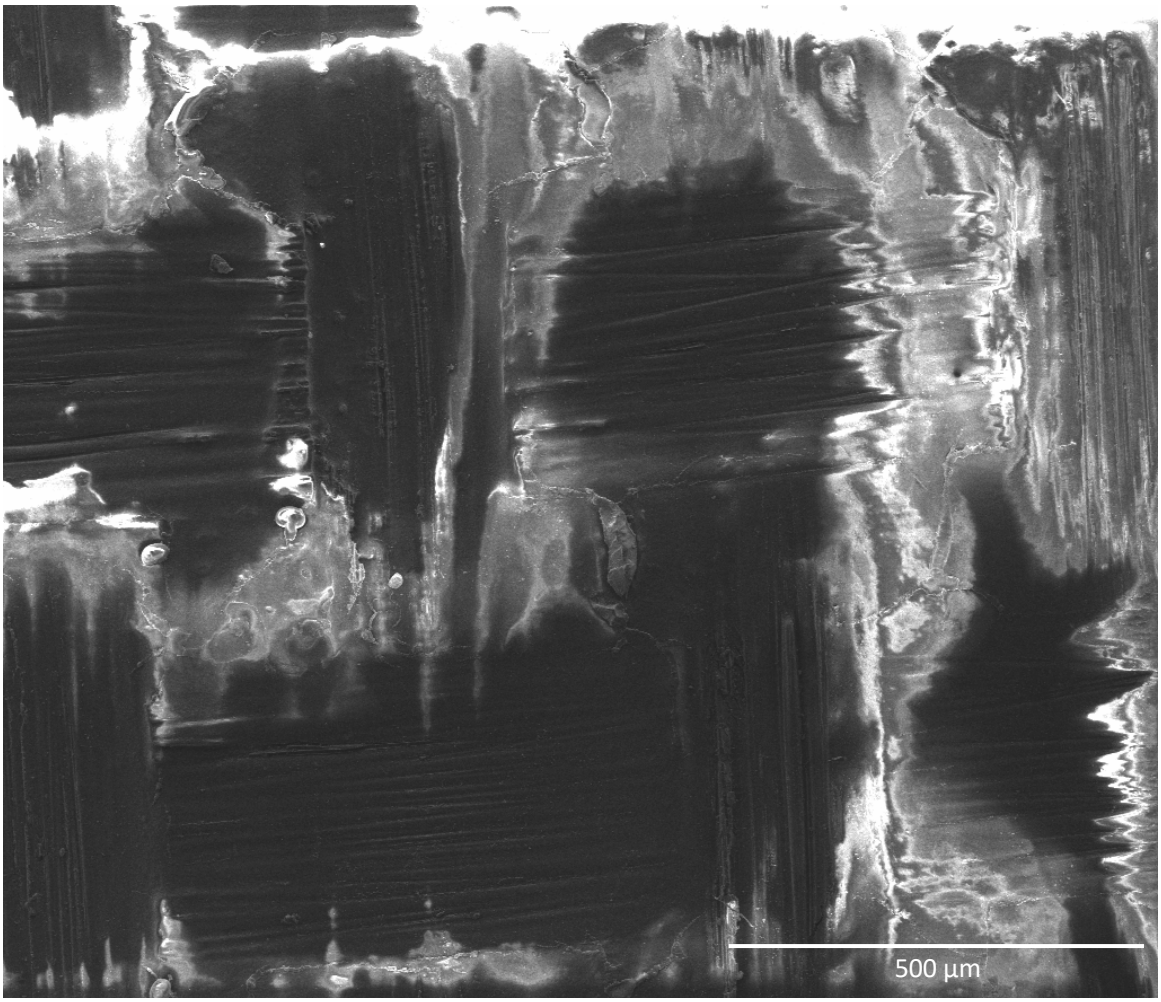

Fig. 4-2 SEM image of virgin CFRP sample at 0 hours

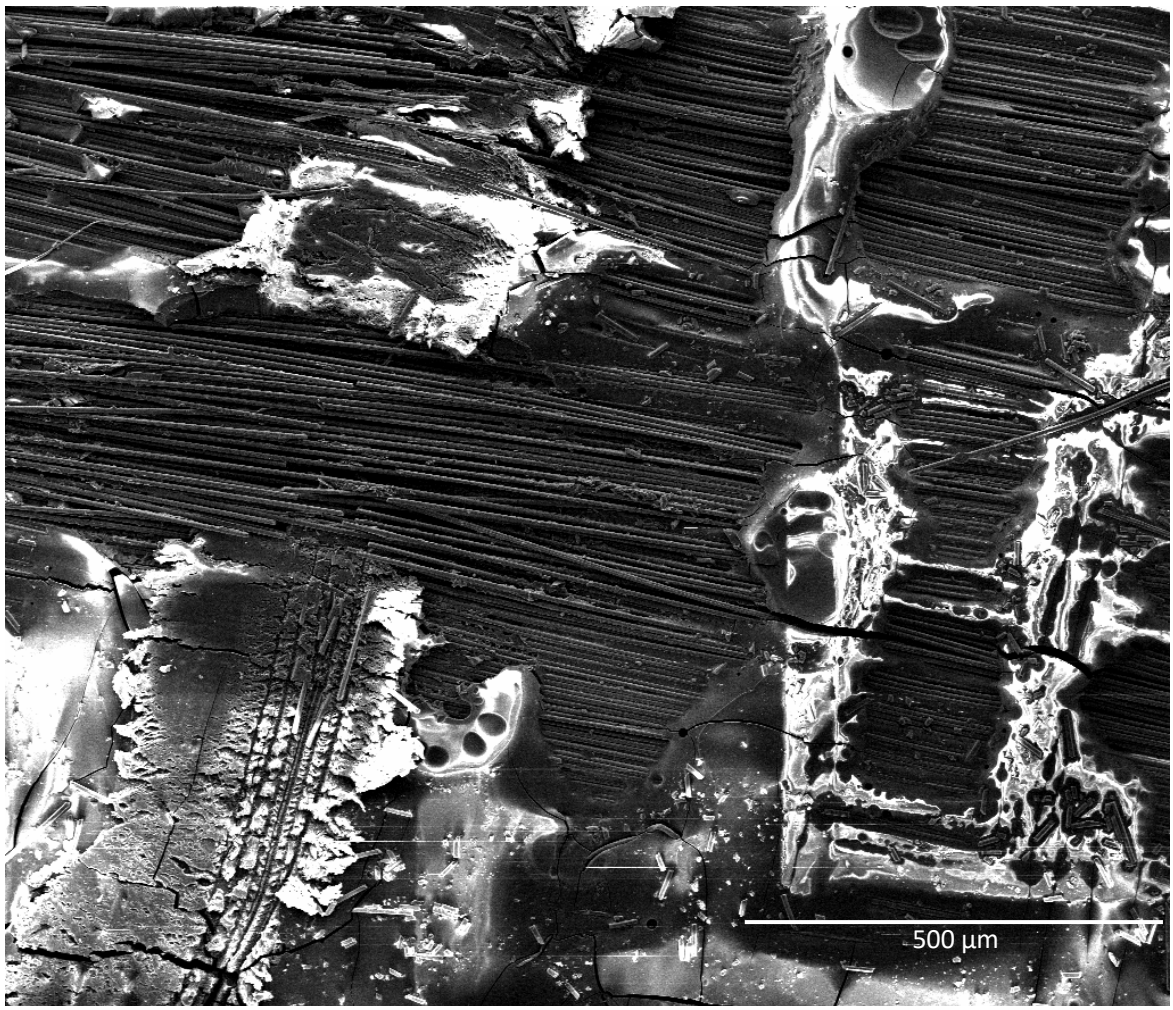

Fig. 4-3 SEM image of CFRP samples after being processed in solution for 2 hours.

Epoxy has been oxidized and dissolved, exposing carbon fibers.

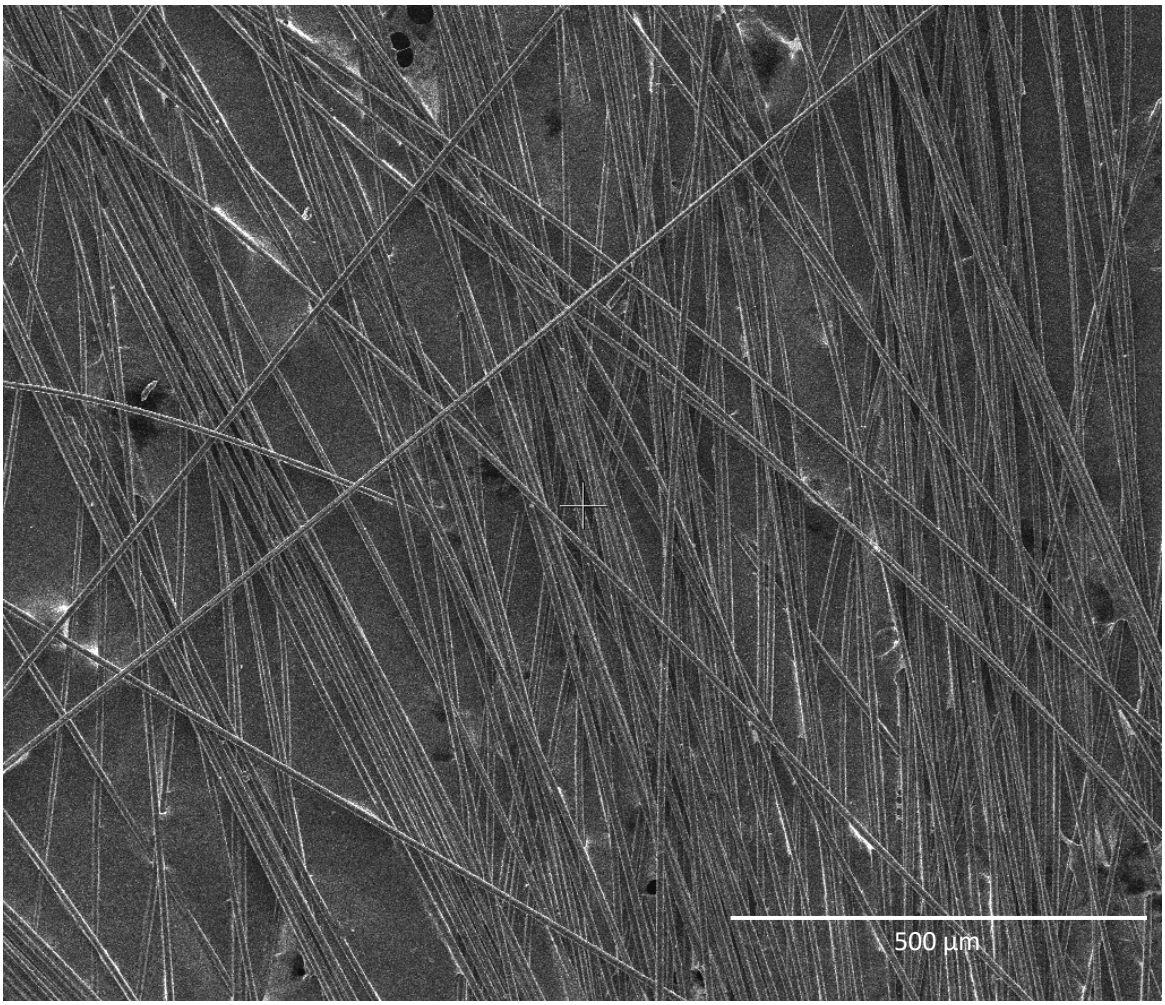

Fig. 4-4 SEM image of fibers recovered from CFRP samples after being processed in solution for 4 hours. Fibers are clean with no epoxy present.

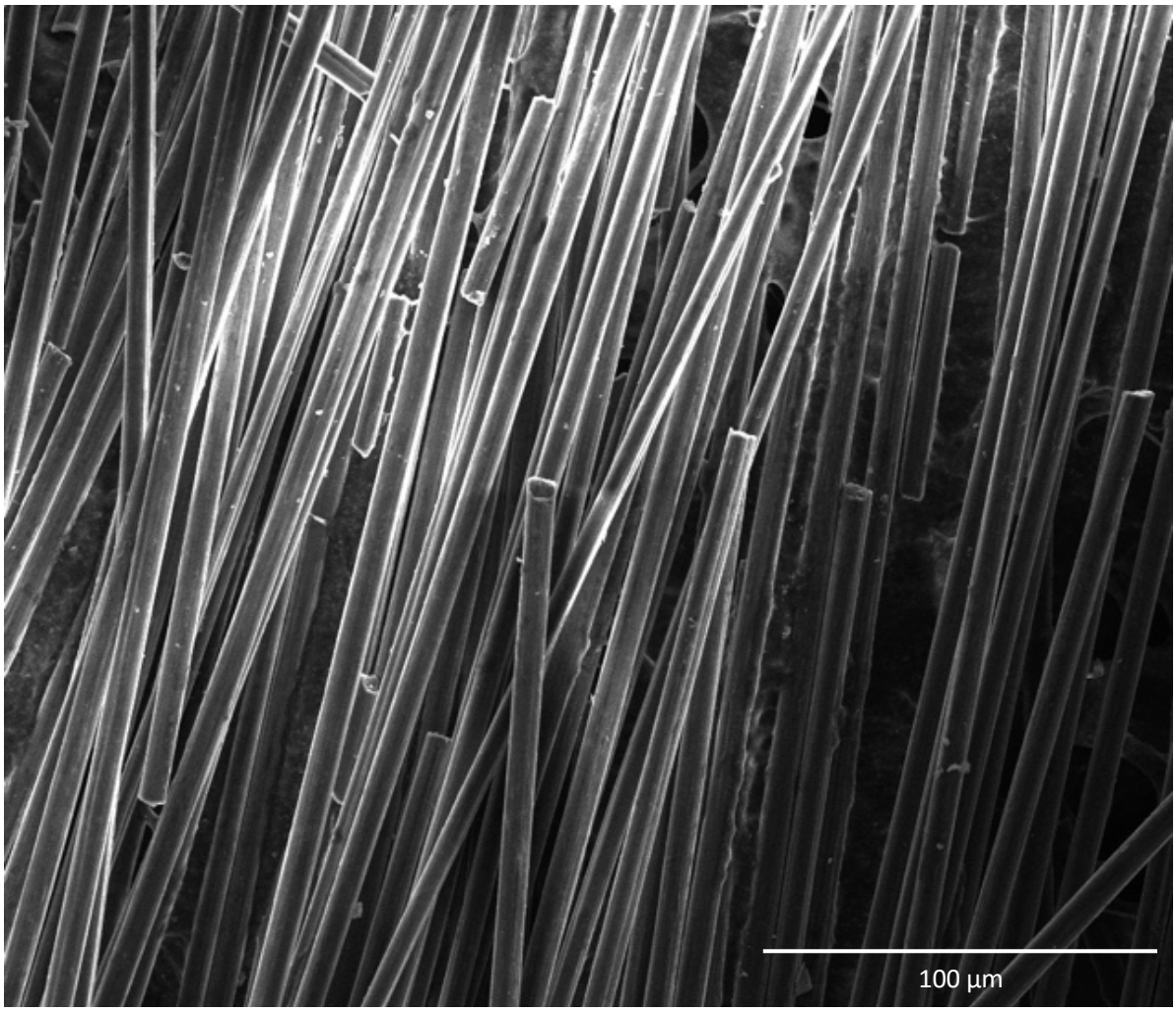

Fig. 4-5 SEM image of virgin fibers

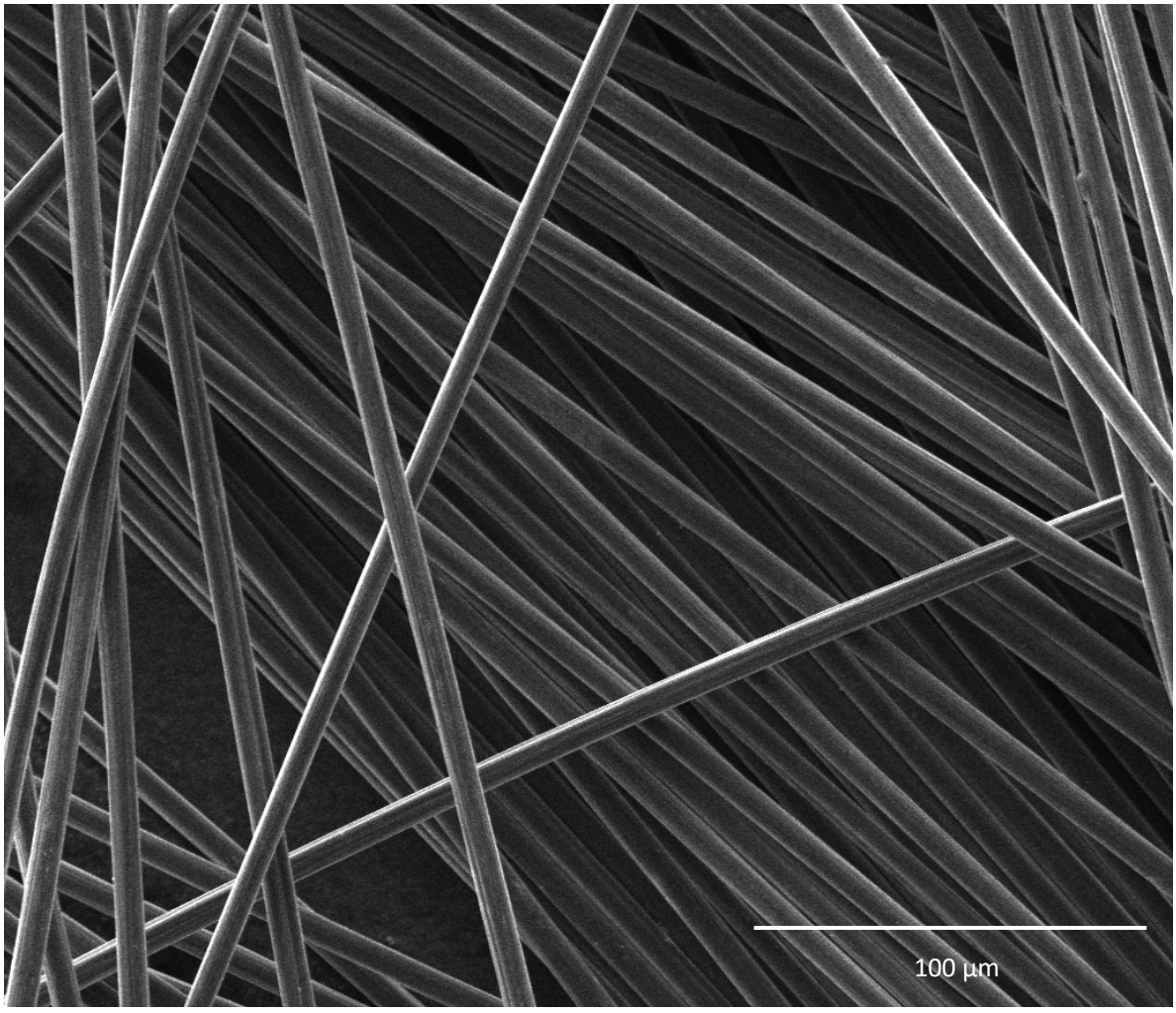

Fig. 4-6 SEM image of fibers recovered at 120°C. Fibers are clean with no epoxy present.

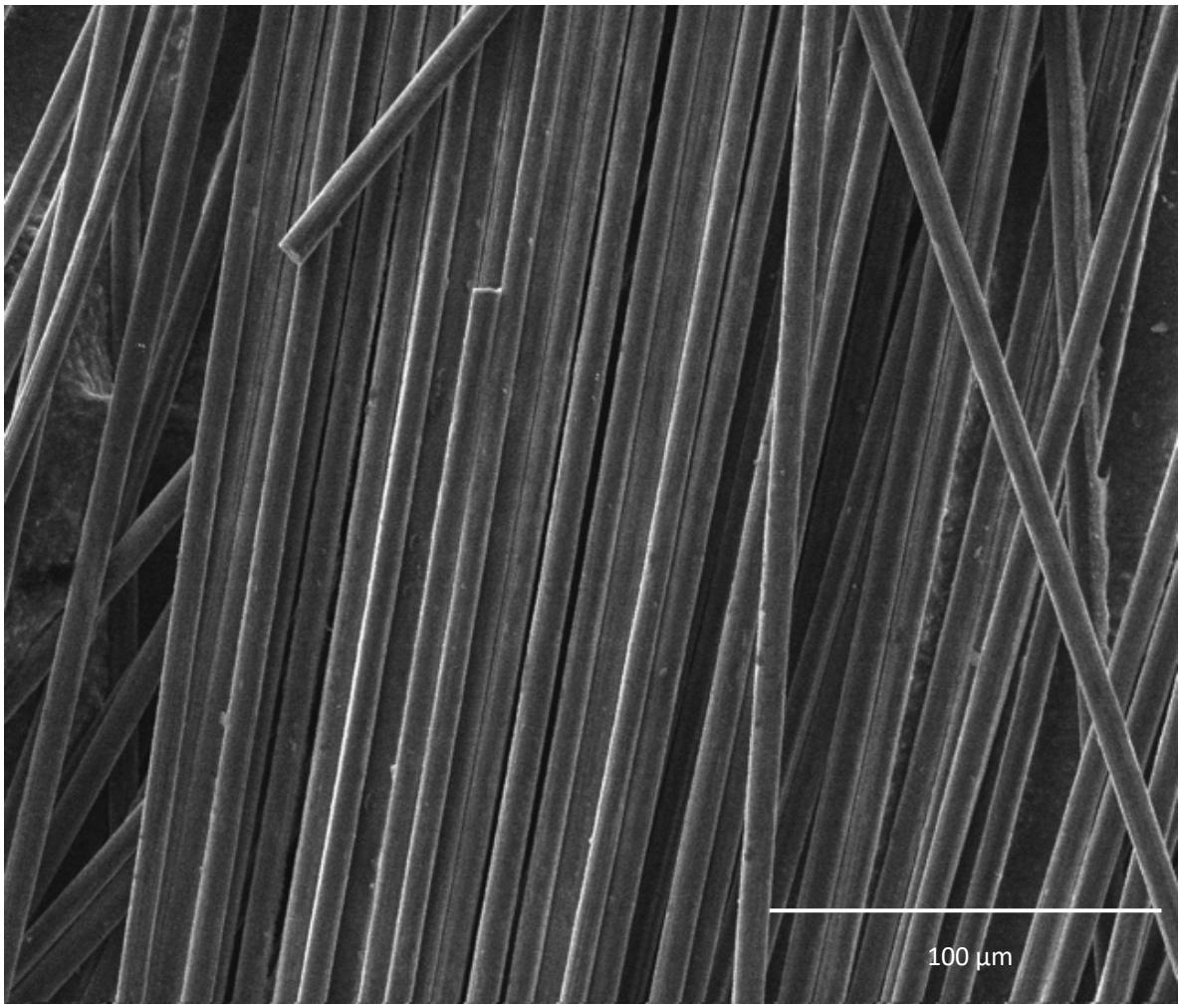

Fig. 4-7 SEM image of fibers recovered at 130°C

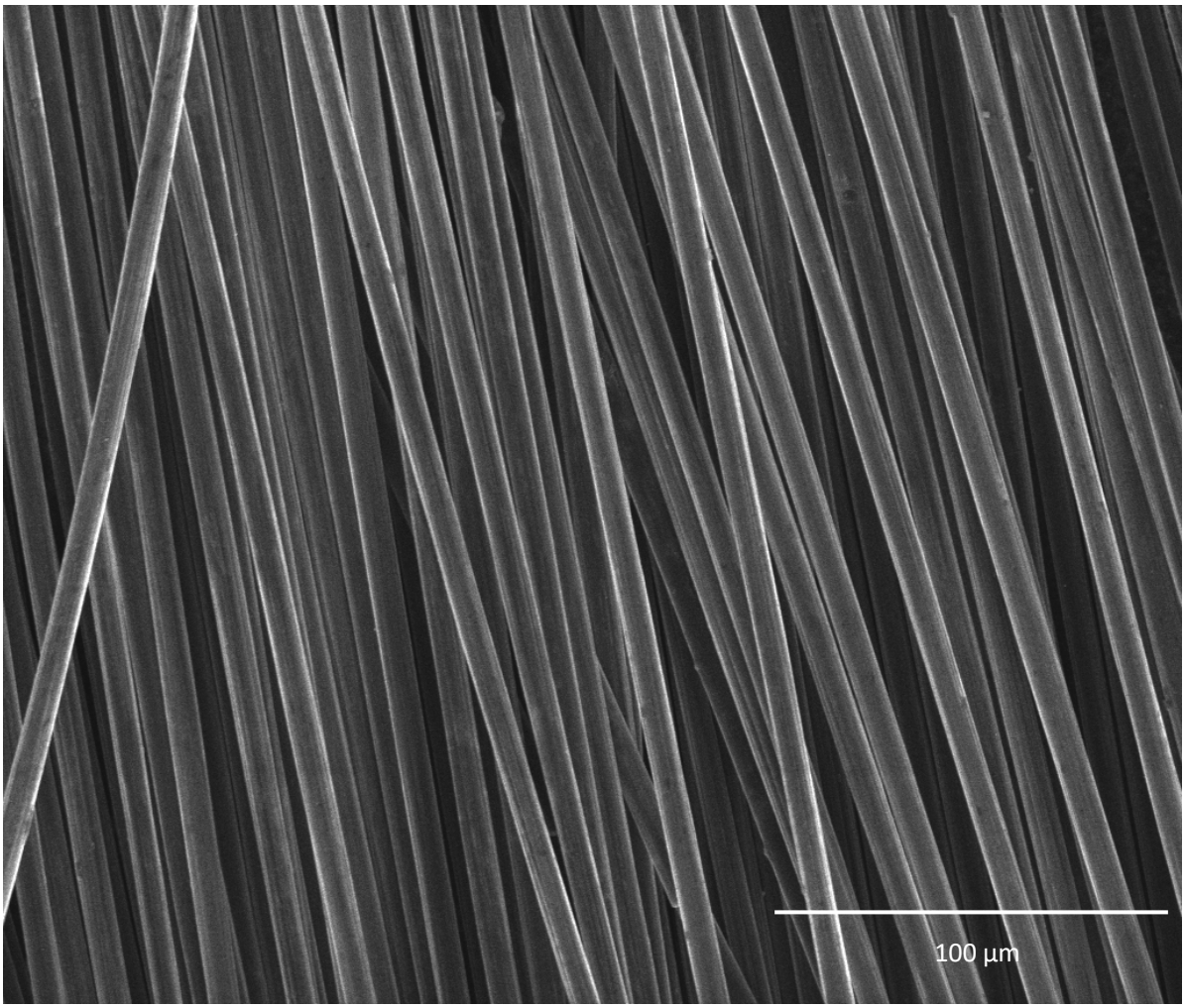

Fig. 4-8 SEM image of fibers recovered at 150°C

Composite and Fiber Chemical Composition

Electron dispersive spectroscopy was used to determine whether epoxy remained in various samples. Figure 4-9 is an EDS analysis of a pristine unprocessed sample. Peaks for both carbon and oxygen were detected, with oxygen being especially indicative of epoxy since carbon fibers should be comprised solely of carbon with no oxygen present. Figure 4-10 is an EDS analysis of a sample processed for 2 hours. This analysis detected only carbon in the regions where no epoxy appeared to be present. In contrast, at sites where epoxy appeared to remain oxygen was detected. Further analysis of fibers recovered from samples are shown in figure 4-11. These samples were processed for 4 hours. EDS detected only carbon with no oxygen. The conclusion of these experiments is that epoxy was successfully removed as a result of the process.

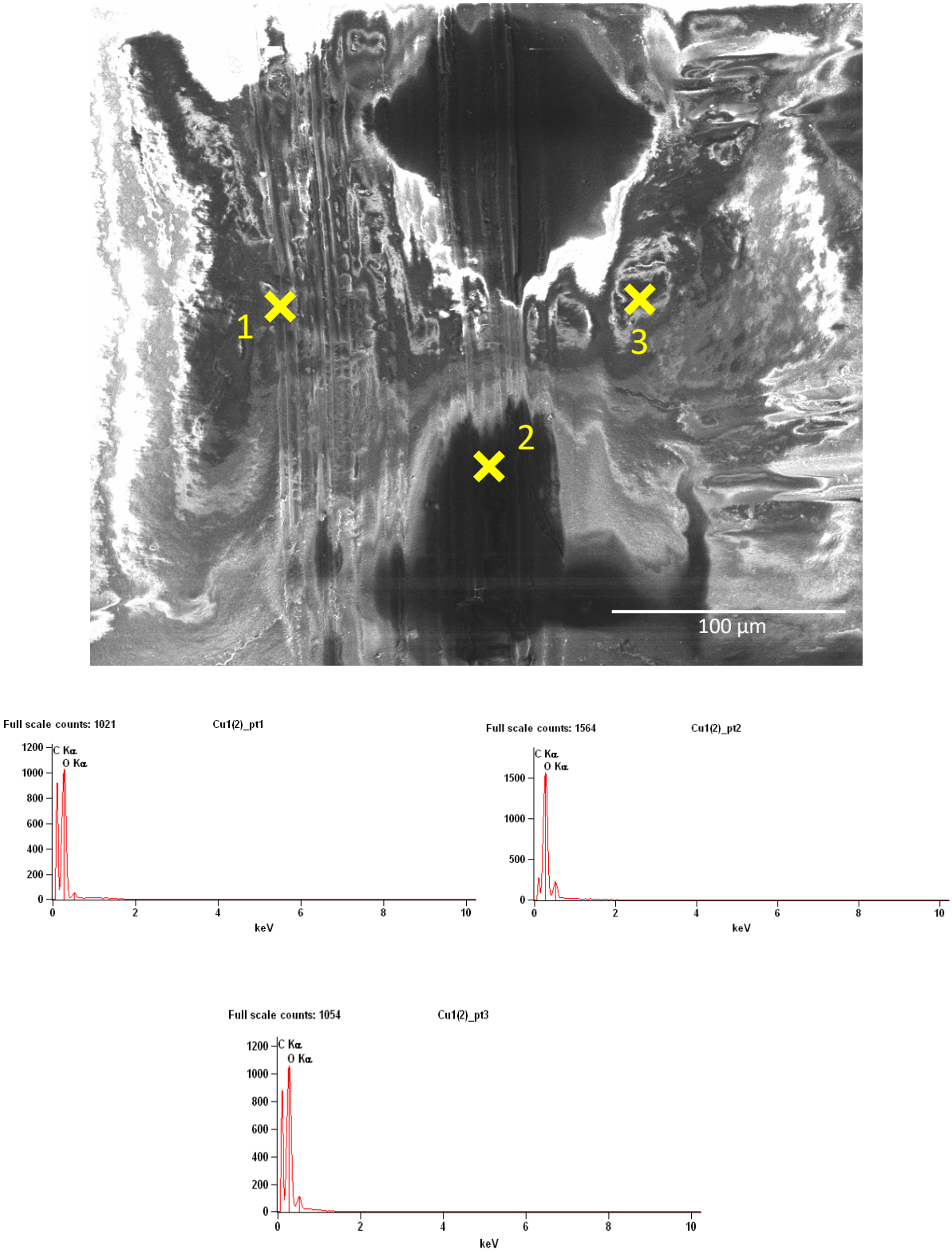

Fig. 4-9 EDS of 3 points on a pristine sample of CFRP. Carbon and oxygen are both detected.

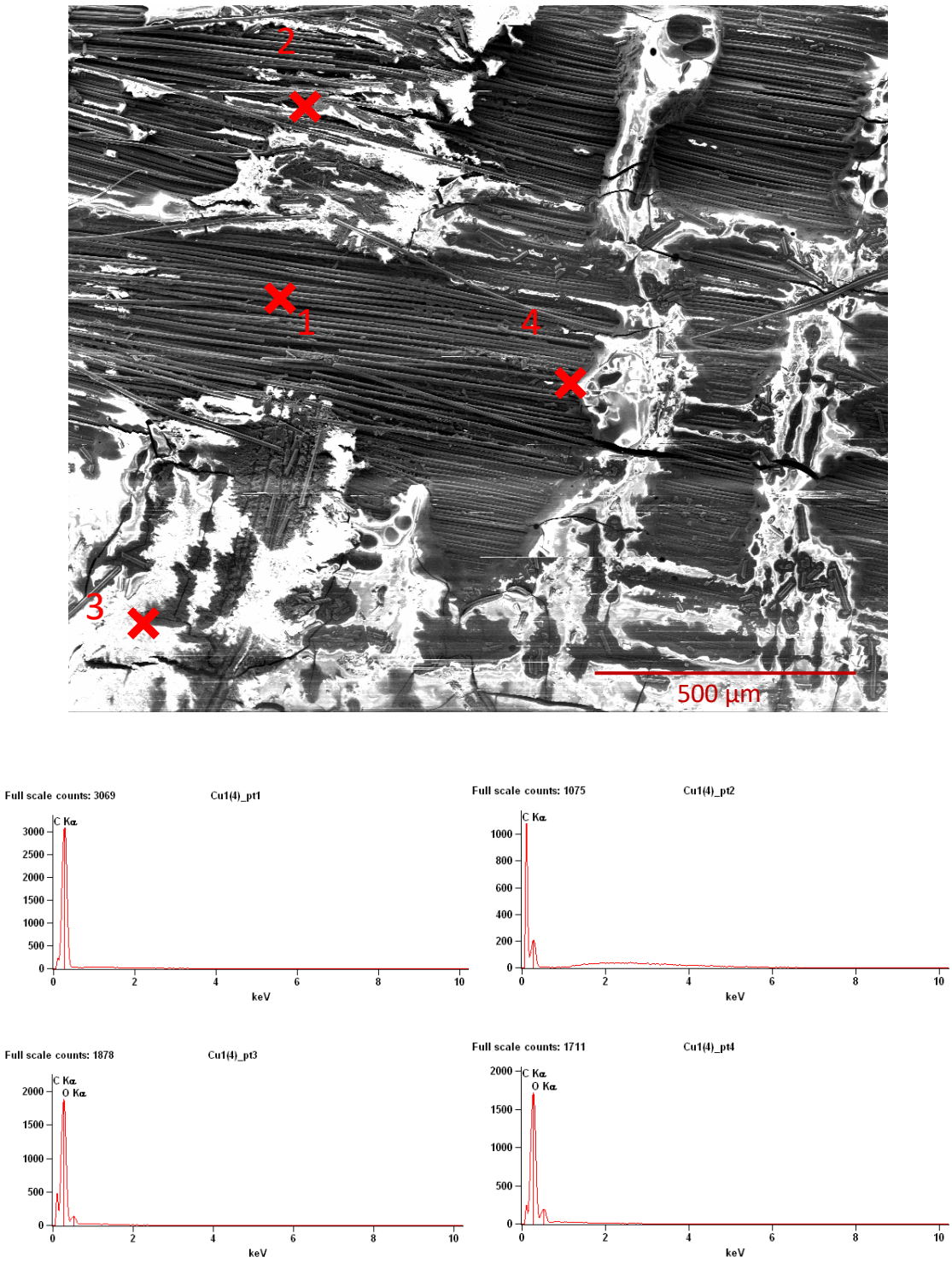

Fig. 4-10 EDS of 4 points on a sample processed for 2 hours. Mostly carbon is detected with some oxygen.

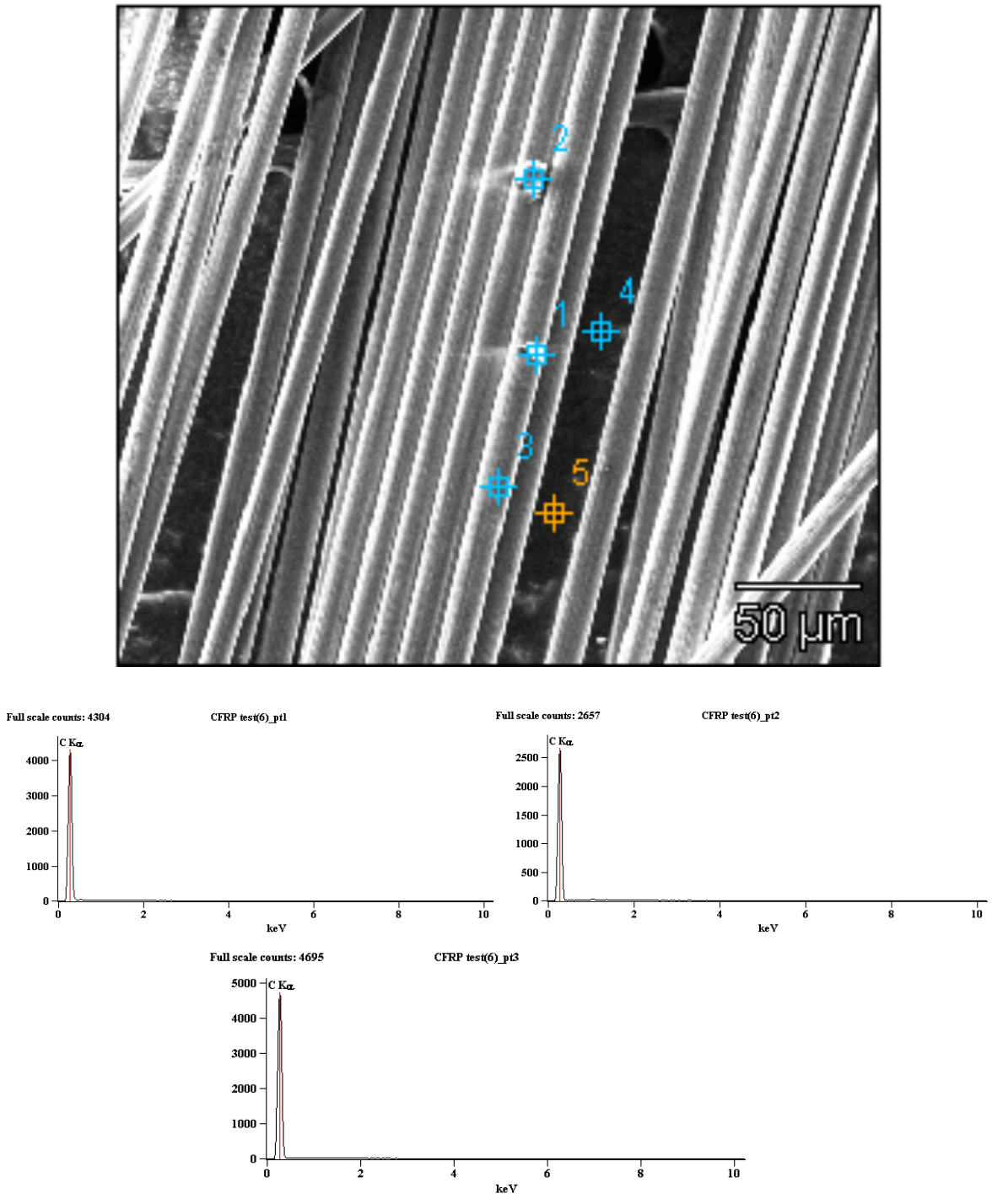

Fig. 4-11 EDS of points on fibers recovered from a sample processed for 4 hours. Only carbon is detected.

Mechanical Strength of Recovered Fibers

An Instron testing machine was used to measure the average tensile strength of the fibers. Figure 4-12 is a collection of the stress-strain curves measured for virgin fibers that had neither been used in composites nor chemically processed. They were measured to have an average strength of 4.11 GPa. Figures 4-13 and 4-14 are stress-strain curves of fibers recovered from samples processed at 120°C and 140°C. They had average strengths of 3.45 GPa and 3.37 GPa and strength losses of 16% and 18% respectively. All measured and calculated values are found in table 4-1. Weibull moduli appeared to be low and standard deviation appeared to be relatively high, but this could be attributed to small sample sizes. Each sample contains thousands of fibers, of which only tens could be tested due to logistical limitations. Figures 4-15 and 4-16 are SEM images taken of fractured fibers. They did not reveal any significant changes in how fracture occurs between virgin and processed fibers. Strength loss could be attributed to a variety of factors including handling of the fibers during composite fabrication, stretching due to epoxy oxidation, or exposure to oxidizing solution. Nevertheless, these values measured indicate good overall strength retention after undergoing the process as well as minimal change in strength due to change in process temperature.

Fiber	Strength (Gpa)	% Change	Weibull
Control	4.11(±0.38)	0	9.64
120°C	3.45(±0.51)	16	3.33
140°C	3.37(±0.37)	18	6.07

Table 4-1 Tensile strength, percentage change, and Weibull moduli for fibers recovered at various conditions

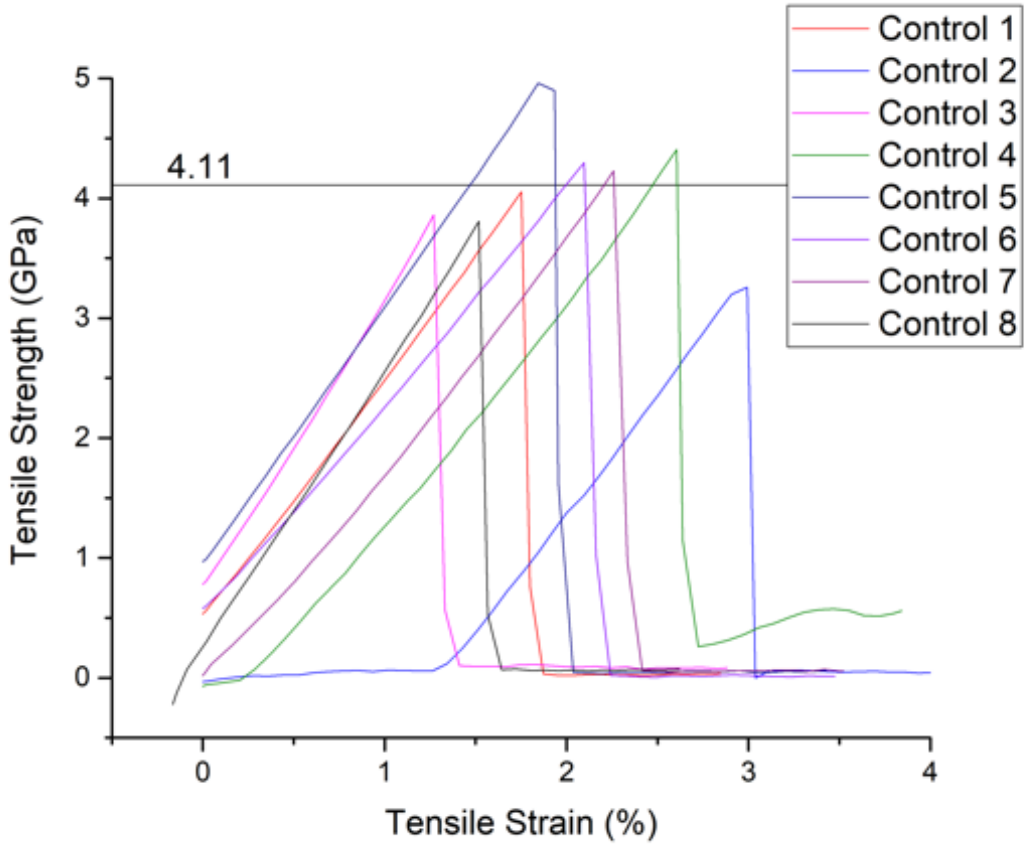

Fig. 4-12 Tensile strength vs strain of virgin fiber samples. Average strength is 4.11 GPa.

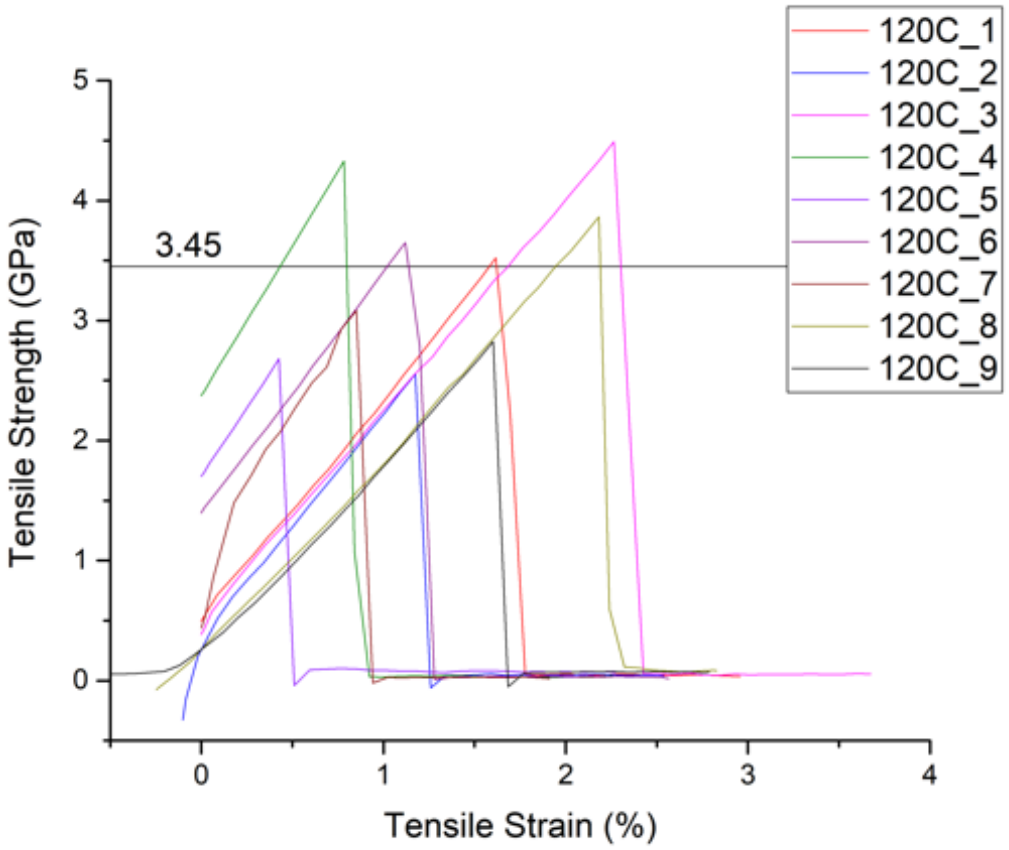

Fig. 4-13 Tensile strength vs strain of recovered fibers from samples processed at 120°C. Average strength is 3.45 GPa.

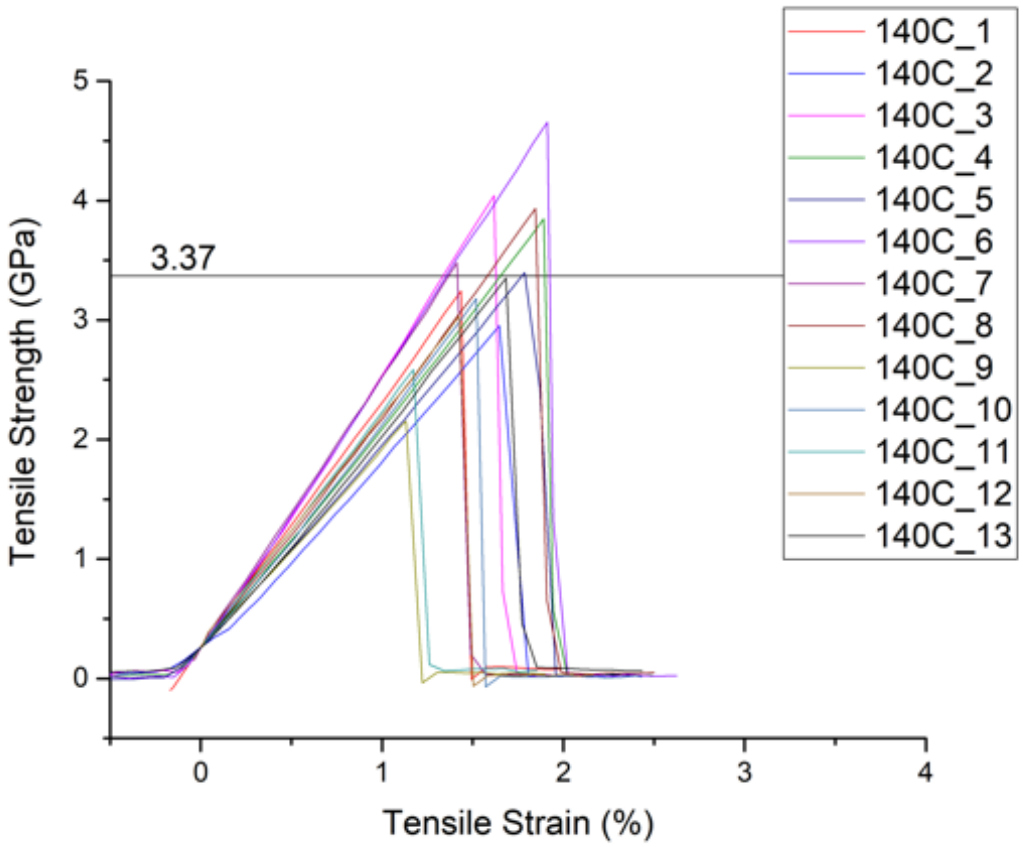

Fig. 4-14 Tensile strength vs strain of recovered fibers from samples processed at 140°C. Average strength is 3.37 GPa.

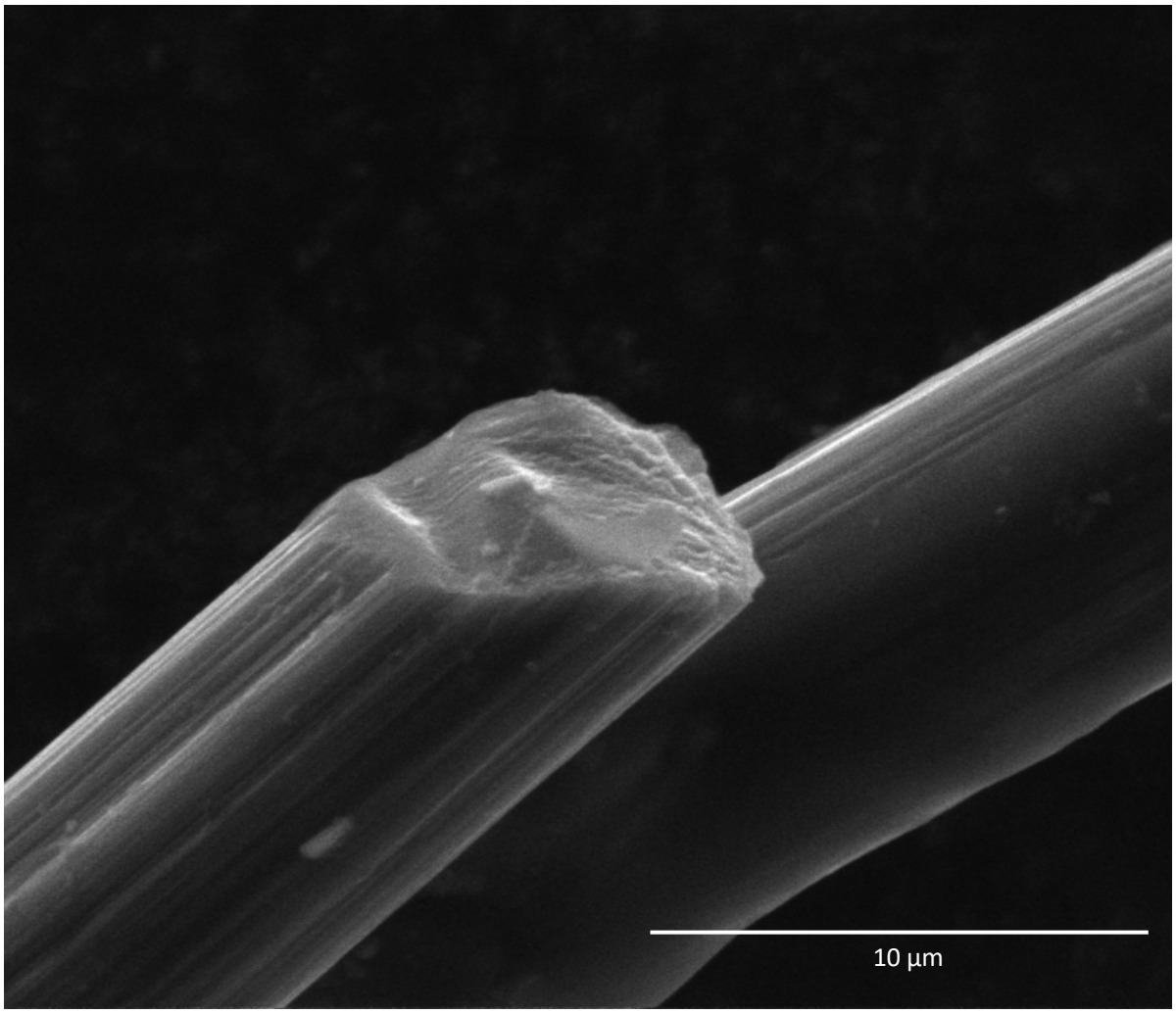

Fig. 4-15 SEM image of fractured virgin fibers

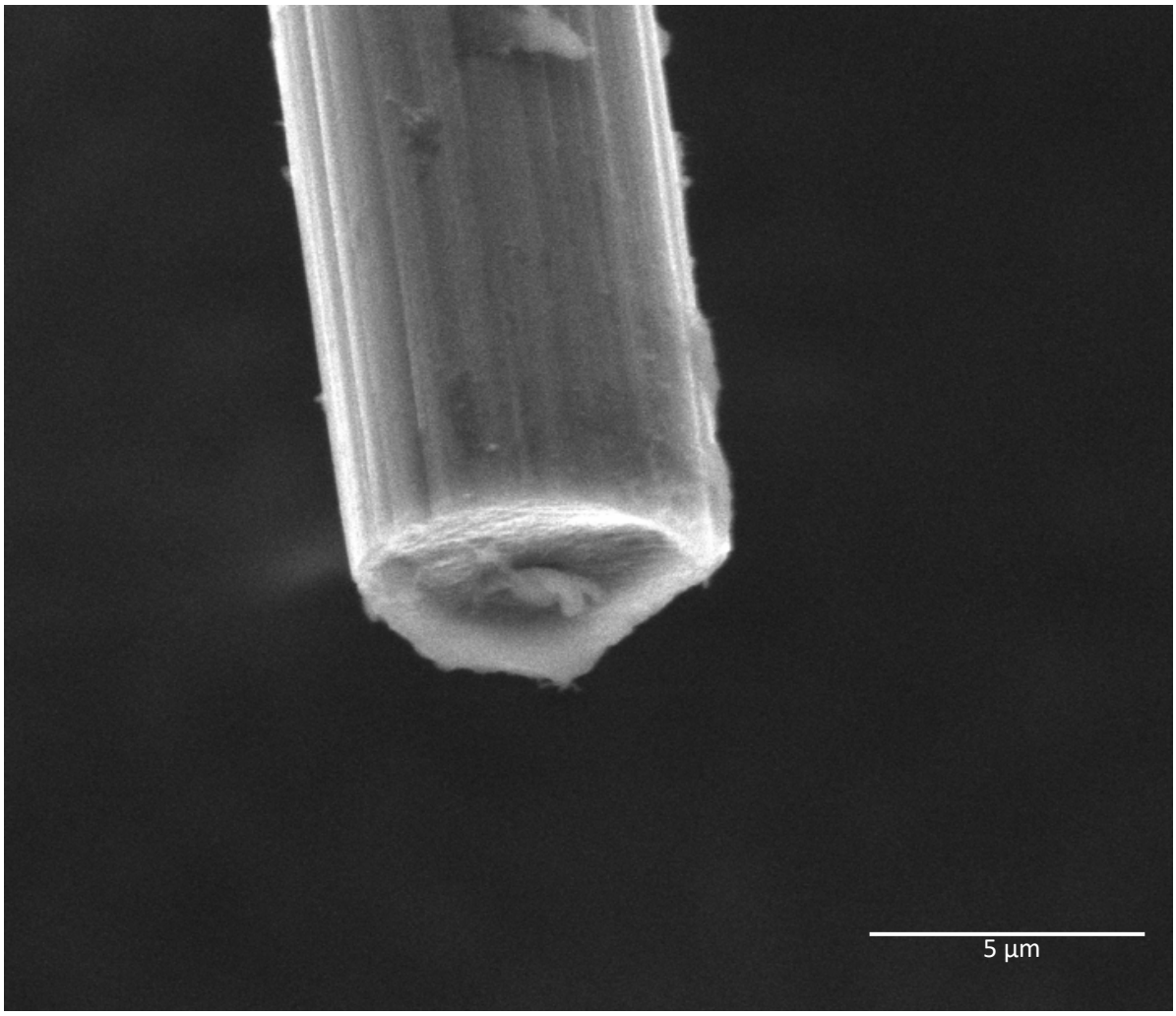

Fig. 4-16 SEM image of fractured fibers: fiber recovered at 120°C

Chemical Composition of Liquid Byproducts

Gas chromatography and mass spectroscopy analysis of the liquid byproduct solution detected a wide variety of small organic compounds. Ethanol, acetaldehyde, and acetic acid were most prevalent. The acetaldehyde and acetic acid can be attributed to the oxidation of ethanol by the hydrogen peroxide and hydroxyl radicals. Many of the other organic compounds are listed in figure 4-17. These compounds are mostly carbon chains containing oxygen or phenyl groups and could feasibly result from the reaction between the radicals formed from the hydrogen peroxide/ethanol solution and the epoxy. The small compounds may have formed due to splitting of the epoxy molecules and rupturing of the rings, as suggested by Reddy et al[37].

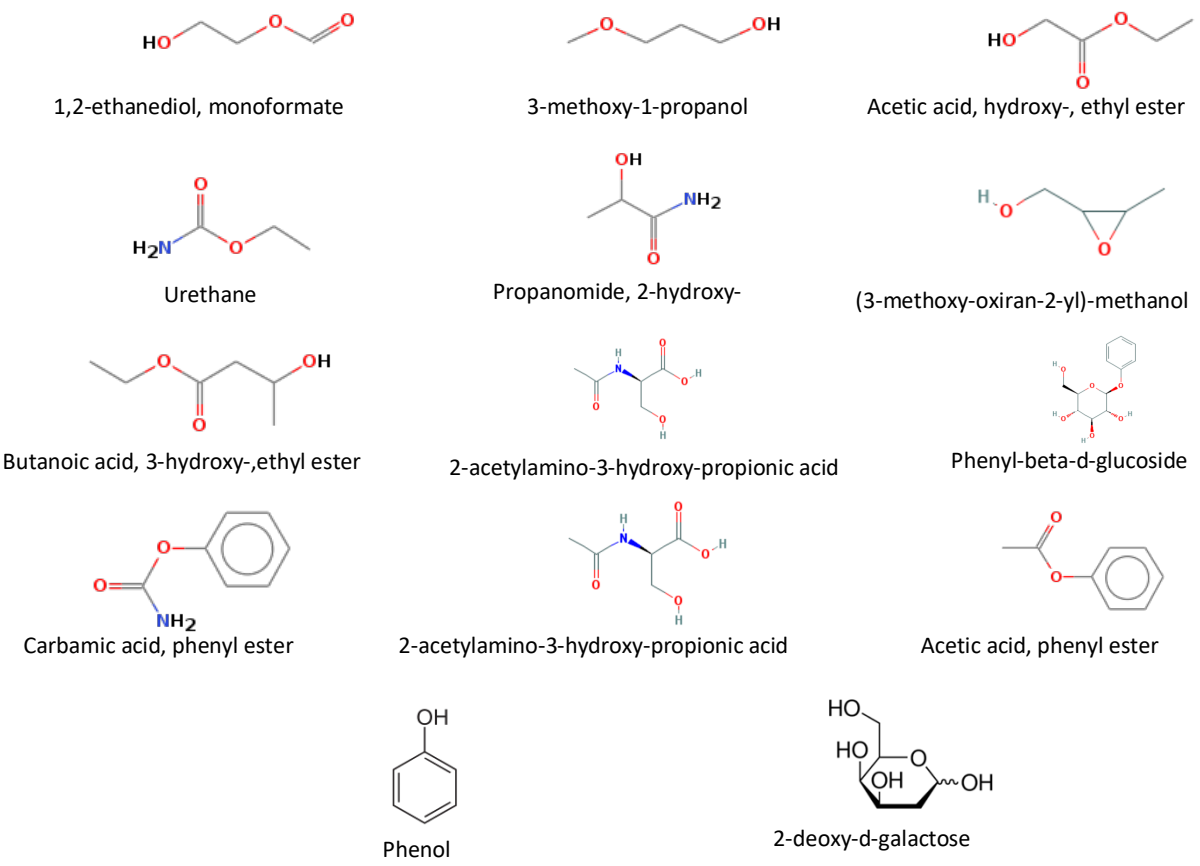

Fig. 4-17 Possible byproducts formed from reaction of epoxy with hydrogen peroxide/ethanol solution

Conclusion

In this section, CFRP samples were processed in the hydrogen peroxide/ethanol solution for various times and temperatures and carbon fibers were recovered from processed samples that had enough epoxy removed. The processed samples and recovered fibers were analyzed via SEM and EDS to determine whether epoxy was still present. Tensile strengths of the recovered fibers were measured and compared to the strength of virgin fibers to determine strength retention after undergoing the process. The liquid byproduct solution remaining after the process was run was analyzed for chemical composition using GCMS.

It was found that after 2 hours, epoxy was clearly oxidized and dissolved from the carbon fiber composite with carbon fibers exposed. After 4 hours a large amount of epoxy was removed, and fibers were released from the composite sample and could also be easily separated and removed from it. These recovered fibers did not appear to have any epoxy remaining on their surfaces. EDS analysis confirmed the removal and absence of epoxy from the composites and fibers due to the detection of only carbon, in contrast to sites with epoxy where oxygen was also detected. The recovered fibers were found to retain 82% – 84% of their original strength. The chemical composition of the liquid byproduct solution contained ethanol and ethanol oxidation products as well as a variety of organic compounds which could be attributed to the result of hydroxyl radicals, ethanol, and epoxy reacting together. None of the detected compounds are known to be highly toxic.

It can thus be determined that the hydrogen peroxide/ethanol solution process was effective at removing epoxy and retaining carbon fiber strength and could be a viable method for recycling and recovering carbon fiber from carbon fiber/epoxy composites. Since it also involves nontoxic compounds and runs at low temperatures, it could also be more easily recommended in

comparison to the other known existing methods, which run at higher temperatures and pressures or involve more dangerous or toxic chemical compounds.

Chapter 5 Development and Verification of Kinetic Model

Introduction

The kinetic model was assumed to follow standard chemical kinetics with the base equation

$$\frac{dC_1}{dt} = a * \exp\left(-\frac{E_a}{RT}\right) * C_2^b * C_3^c$$

where dC_1/dT refers to change in concentration over time of the primary component in question (in this case the carbon fiber/epoxy composite), a refers to a general fitting variable, E_a is the activation energy, R is the gas constant, and T is temperature. C_2 and C_3 refers to the concentrations of chemical reactants, in this case hydrogen peroxide and ethanol. Since the main component affected is a solid, change in concentration (C_1) was instead modified to change in mass. Surface area exposed to the solution would also affect the rate of reaction since the composite is not evenly distributed throughout the solution as a liquid, so it was also added to the base equation. With these modifications the equation becomes

$$\frac{dM}{dt} = a * \exp\left(-\frac{E_a}{RT}\right) * [H_2O_2]^b * [EtOH]^c * d * SA$$

With the exception of constant a, a mass loss rate was found for varying values of each parameter while keeping the other parameters static. A fitting was then calculated for graphs of the rate plotted against each parameter/variable in order to determine the value of its corresponding constant (E_a, b, c, d).

Effects of Temperature

The effects of temperature on the reaction was analyzed by varying temperature between 120°C and 150°C in 10°C increments. The oxidizing solution used in all experiments was 10 mL hydrogen peroxide solution (30% vol. in water) mixed with 20 mL ethanol (100% pure). Figures 4-16, 5-1, 5-2, and 5-3 are graphs plotting the amount of mass dissolved from composite samples over time at respective process temperatures of 120°C, 130°C, 140°C, and 150°C. Linear equations were fit to each data set to determine the rate at which mass was lost over time. Nonzero y-intercepts are present in each fit equation but ignored to account for the time needed for the reactants and reactor vessel to reach reaction temperature. It can be seen that with increasing temperature the rate of dissolution increases, starting at 0.367 g/hr at 120°C then increasing until reaching 1.012 g/hr at 150°C.

This increase in the rate with temperature can be intuitively explained by considering that higher temperatures result in an increase an average energy and therefore more chemical interactions between the radical groups and the epoxy with enough energy to meet the activation energy requirements for a reaction to occur. It should also be noted that increasing the temperature will also increase the rate at which hydrogen peroxide degrades into oxygen and hydrogen[7]. With this increase in hydrogen decomposition, it should be expected that at a high enough temperature the rate of mass loss will decrease due to a loss in hydroxyl radicals.

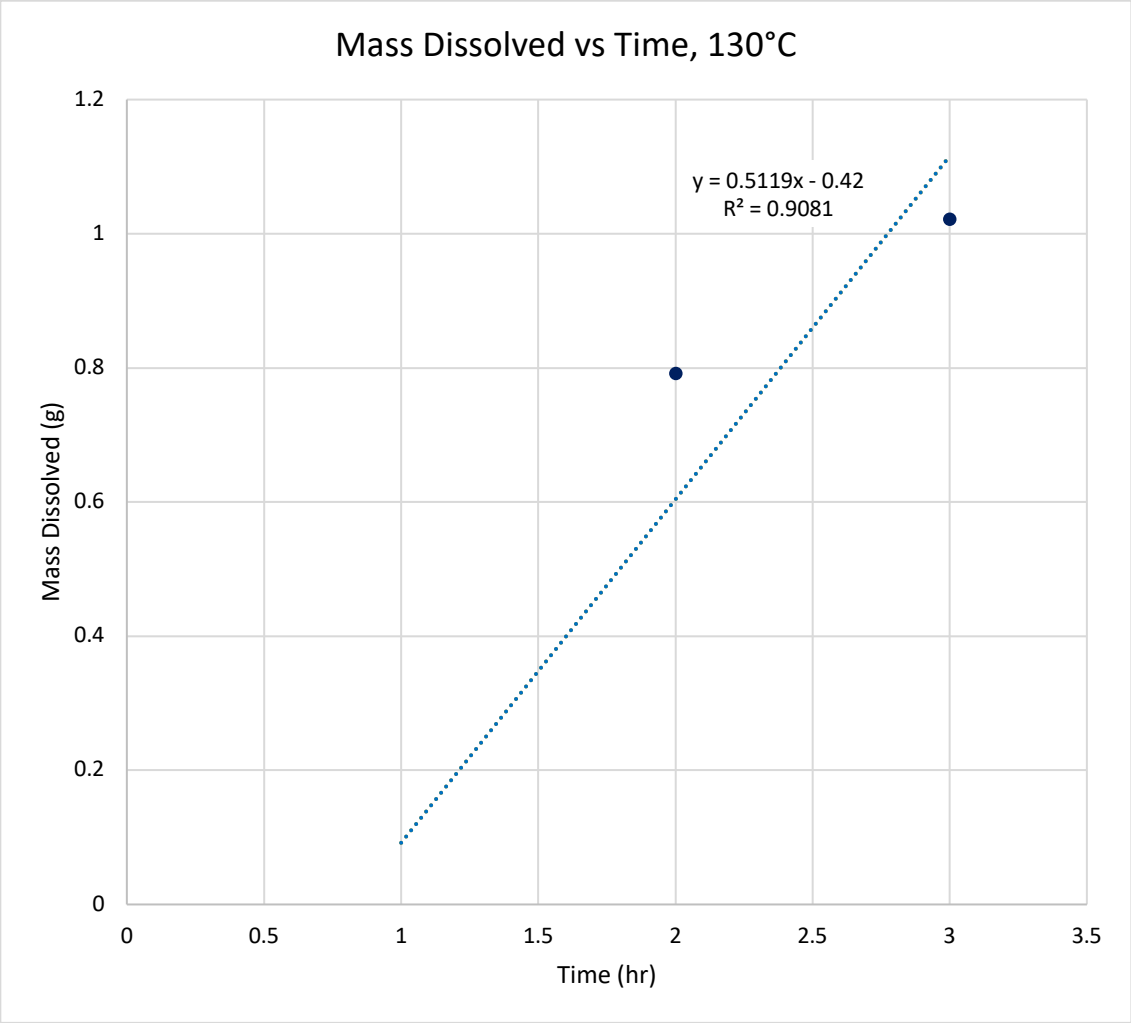

Fig. 5-1 Change in mass plotted against time, 130°C. Estimated 0.5119 g dissolved per hour, with offset for heating to reaction temperature.

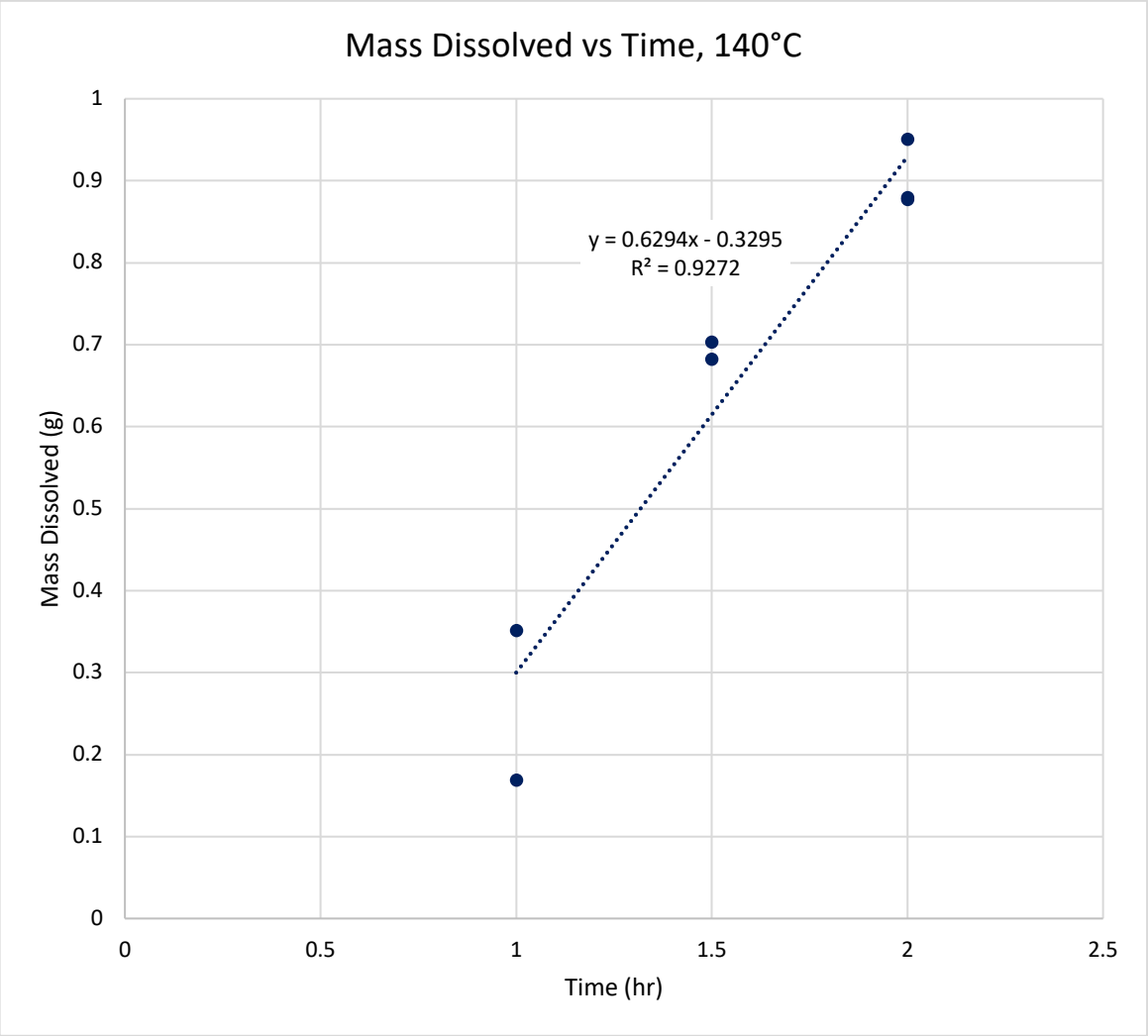

Fig. 5-2 Change in mass plotted against time, 140°C. Estimated 0.6294 g dissolved per hour, with offset for heating to reaction temperature.

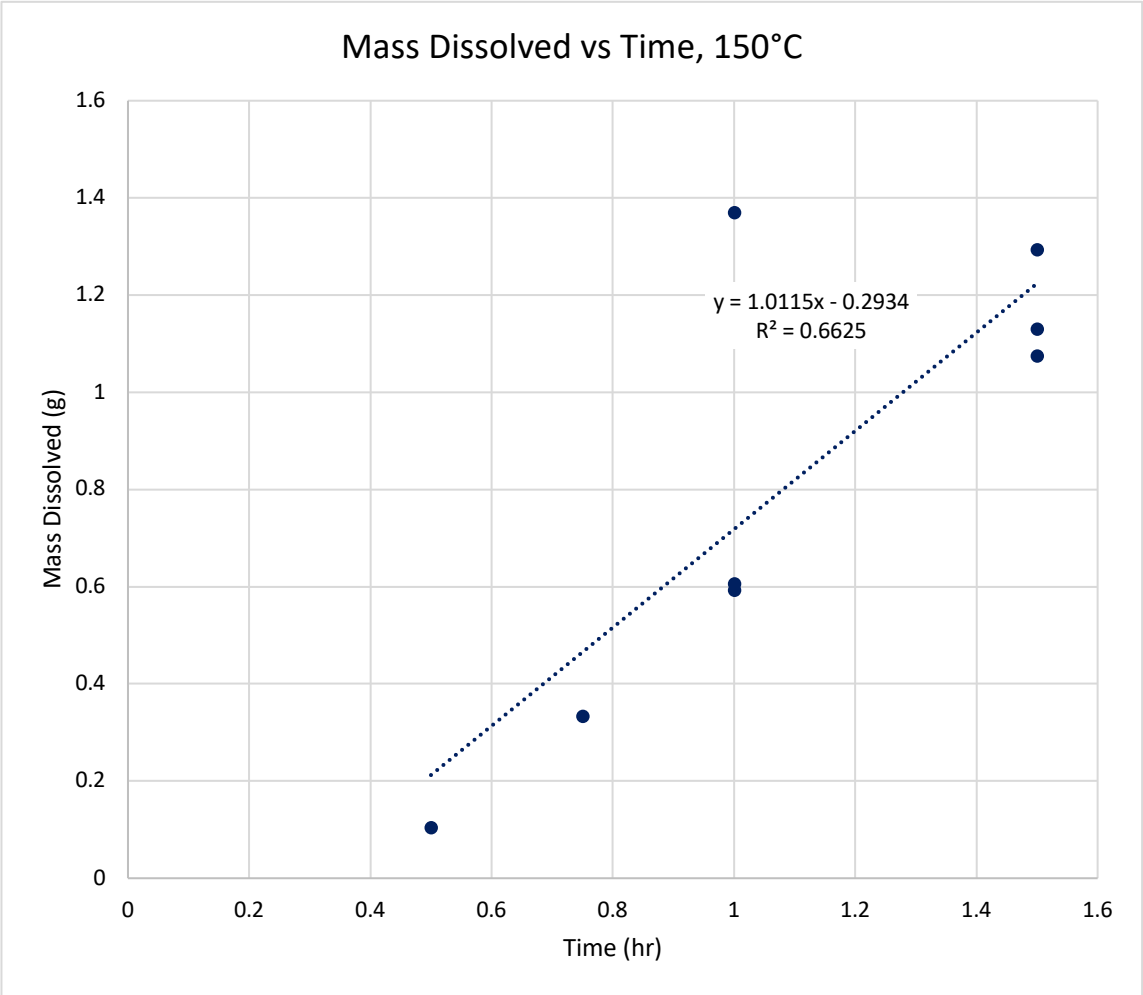

Fig. 5-3 Change in mass plotted against time, 150°C. Estimated 1.0115 g dissolved per hour, with offset for heating to reaction temperature.

Fitting an exponential function to the graph in figure 5-4 with rate plotted against inverse temperature had good correlation with an R^2 value of 0.9718. The fitted equation should be equivalent to the Arrhenius relation, e.g.

$$\mathrm{a} * \exp\left(-\frac{E_a}{RT}\right) = 323142 \exp\left(-\frac{5390}{T}\right)$$

$$\frac{E_a}{R} = 5390$$

$$E_a = 44812.46 \frac{\mathrm{J}}{\mathrm{mol} * \mathrm{K}}$$

Using a gas constant R value of 8314 J/mol*K, the activation energy was thus calculated to be 44812.46 J/mol*K.

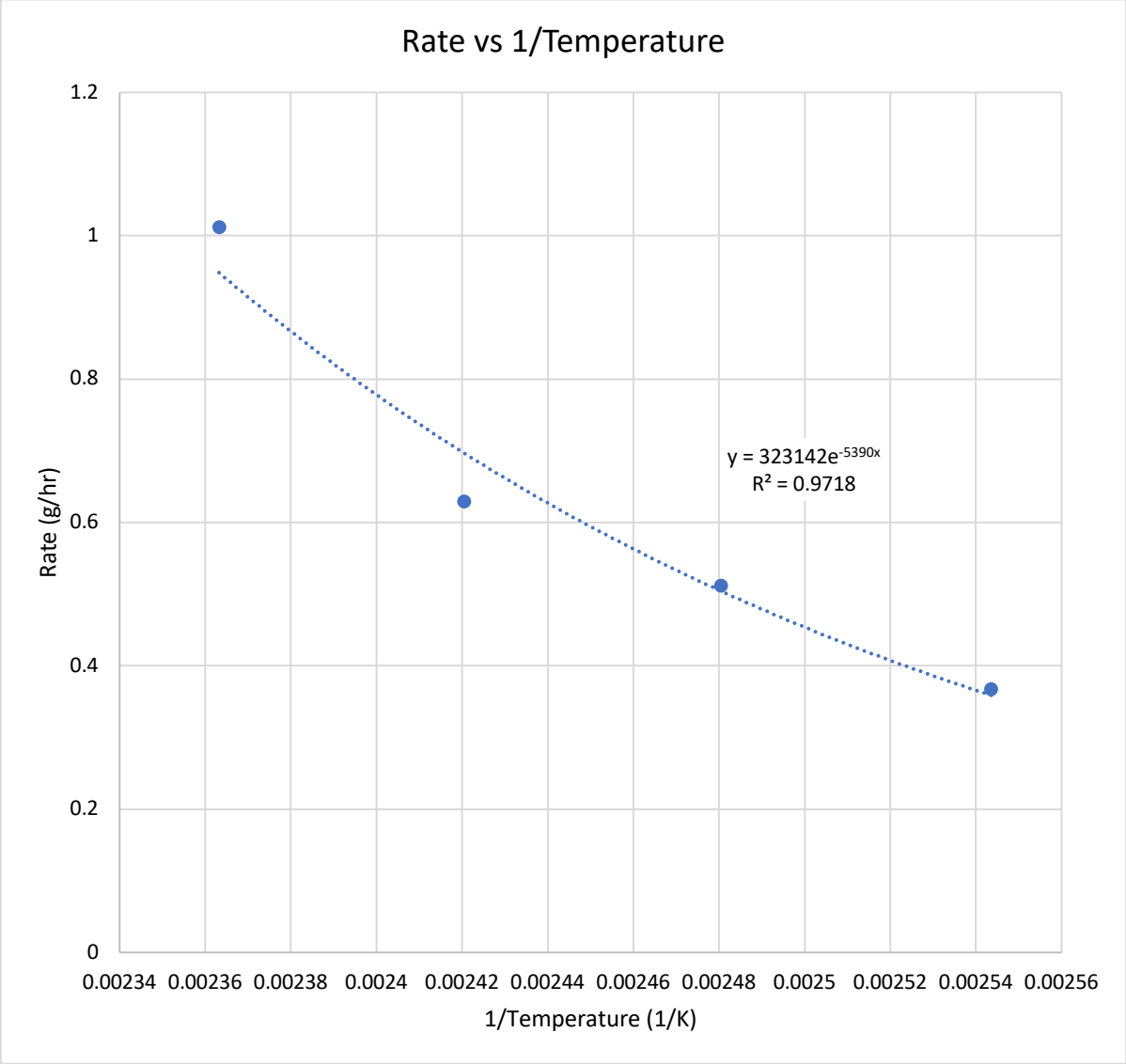

Fig. 5-4 Mass dissolution rates plotted over inverse temperature. Fit is modeled after Arrhenius relation.

Effects of Hydrogen Peroxide Concentration

The dependence of the reaction on concentration of hydrogen peroxide was determined by mixing various volumes of hydrogen peroxide solution with 5 mL ethanol, while adding deionized water to maintain a total volume of 30 mL. Figures 5-5, 5-6, and 5-7 plot the decrease in mass over time for samples processed in solutions with volumetric percentages of 33%, 66% and 50% hydrogen peroxide, respectively. It can be seen that with increasing concentration of hydrogen peroxide the rate of mass dissolution increases. At 33% volumetric (3.257 *M*), the rate is determined to be 0.060 g/hr. The rate increases to 0.250 g/hr at 50% volumetric (4.885 *M*) and then to 0.395 g/hr at 66% volumetric (6.513 *M*). Figure 5-8 is the graph of rate of mass lost per hour plotted against concentration of hydrogen peroxide. It appears that with an increase in concentration the rate of mass dissolution increases. This could be explained with an increase in concentration resulting in the presence of more hydrogen peroxide molecules and therefore more radical organic compounds to react with and degrade the epoxy. Fitting a power function and comparing to the hydrogen peroxide portion of the model, the constant *b* can be calculated as:

$$a * [H_2O_2]^b = 0.0024x^{2.784}$$

$$b = 2.784$$

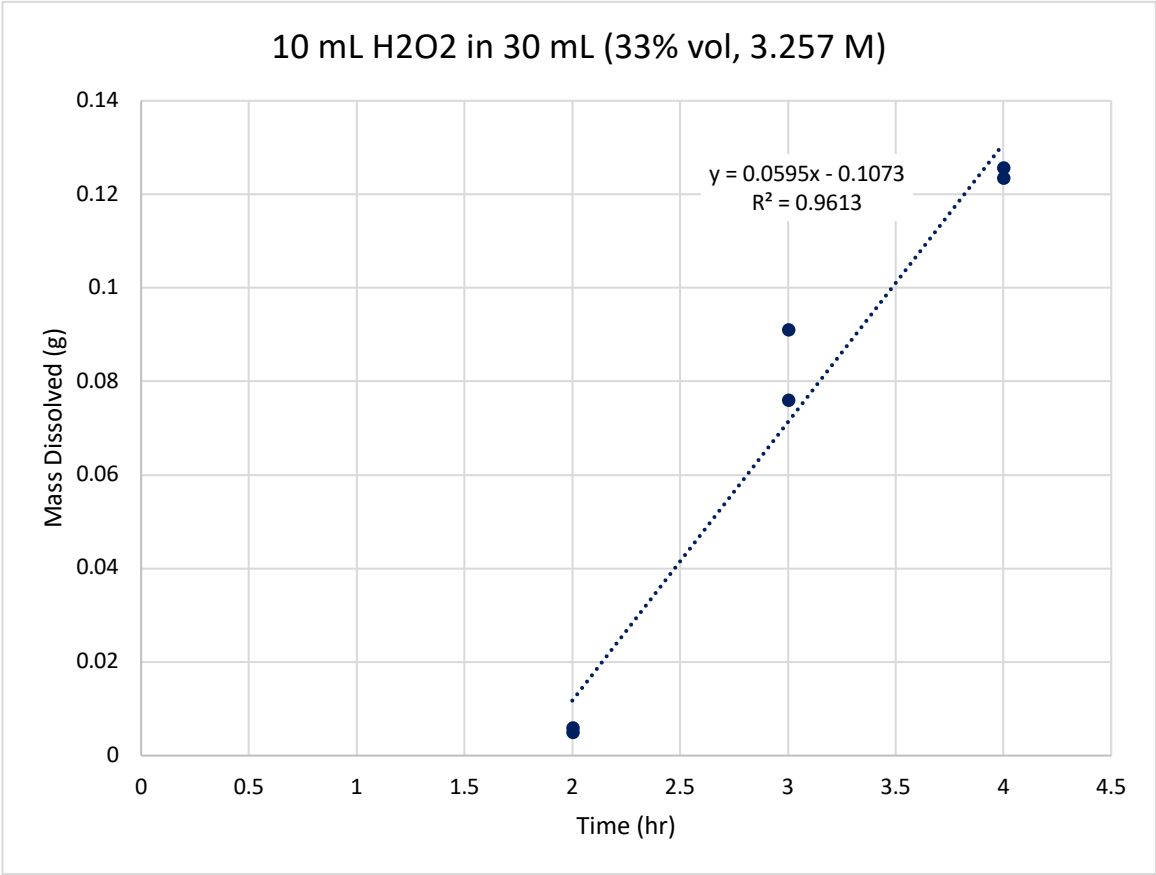

Fig. 5-5 Change in mass plotted over time, 33 vol% H_2O_2. Estimated 0.595 g dissolved per hour, with offset for heating to reaction temperature.

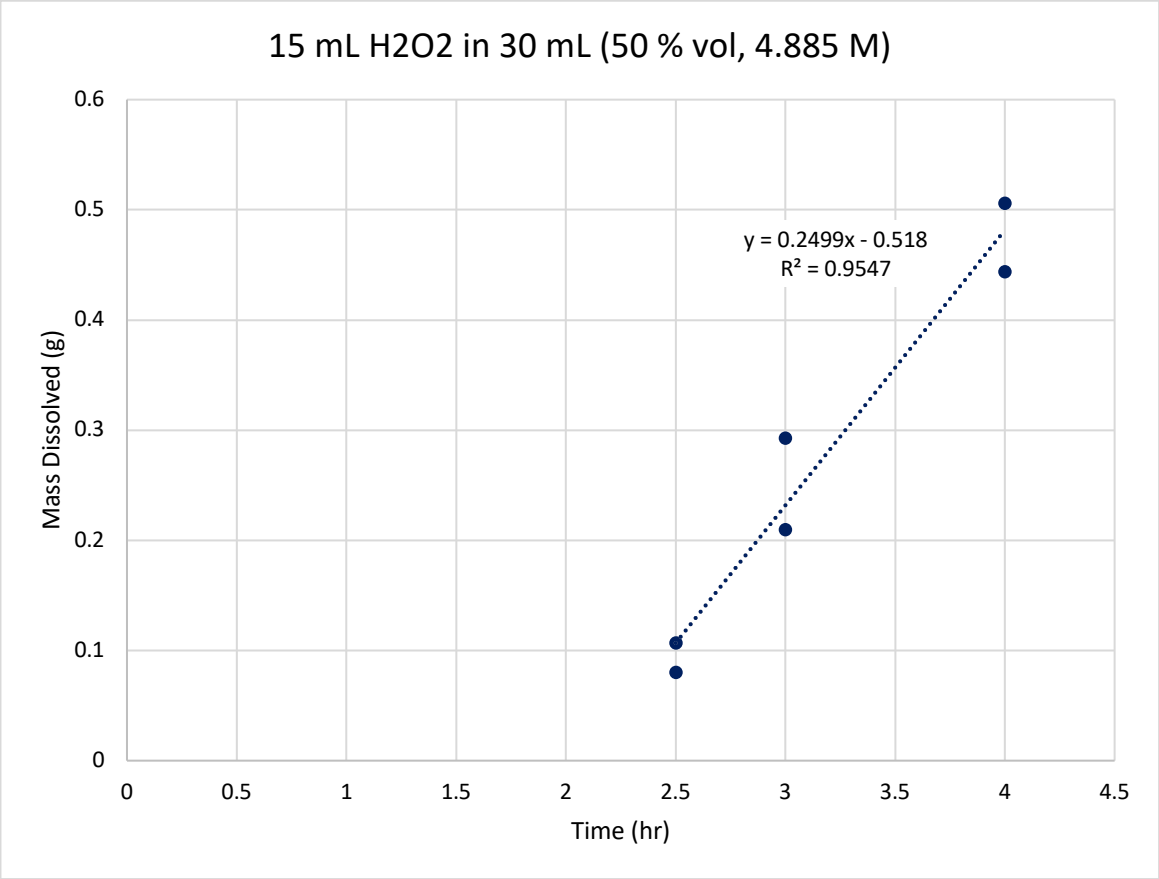

Fig. 5-6 Change in mass plotted over time, 50 vol% H_2O_2. Estimated 0.2499 g dissolved per hour, with offset for heating to reaction temperature.

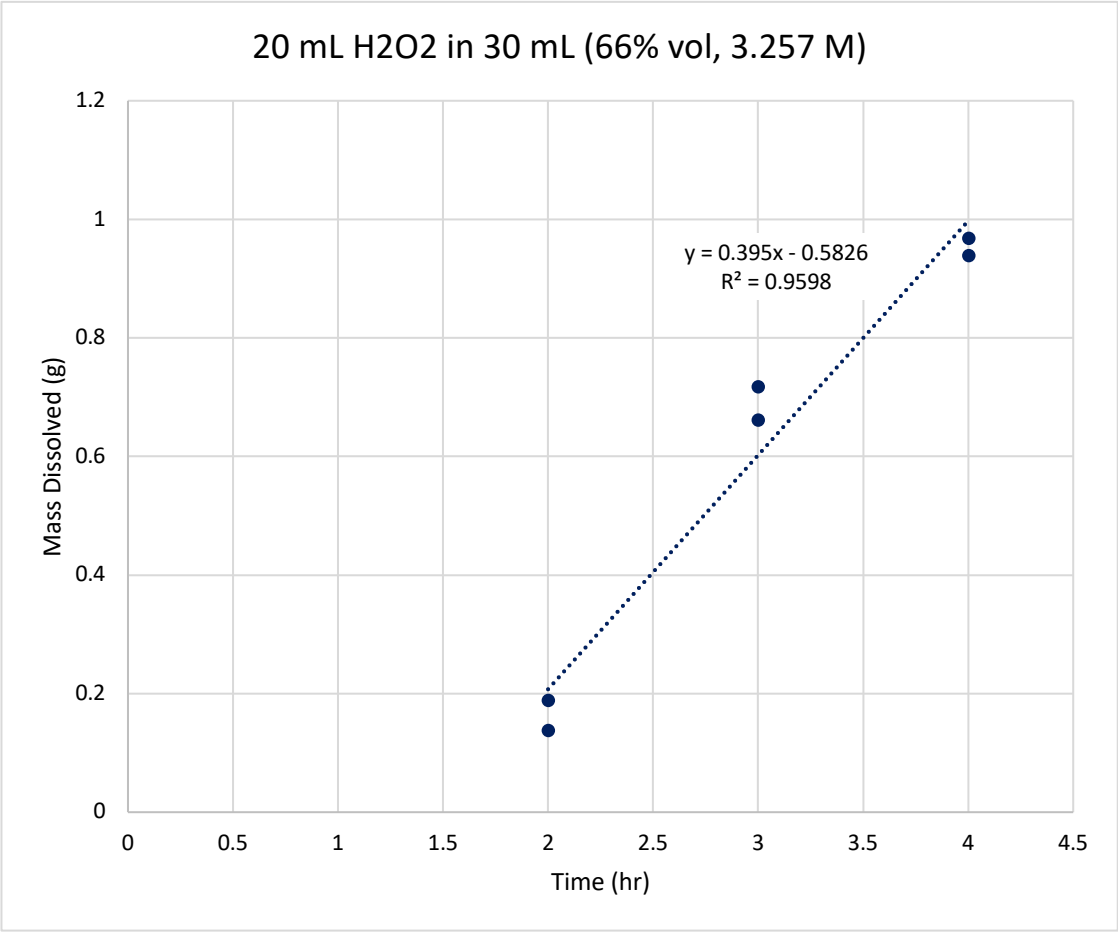

Fig. 5-7 Change in mass plotted over time, 66 vol% H_2O_2. Estimated 0.395 g dissolved per hour, with offset for heating to reaction temperature.

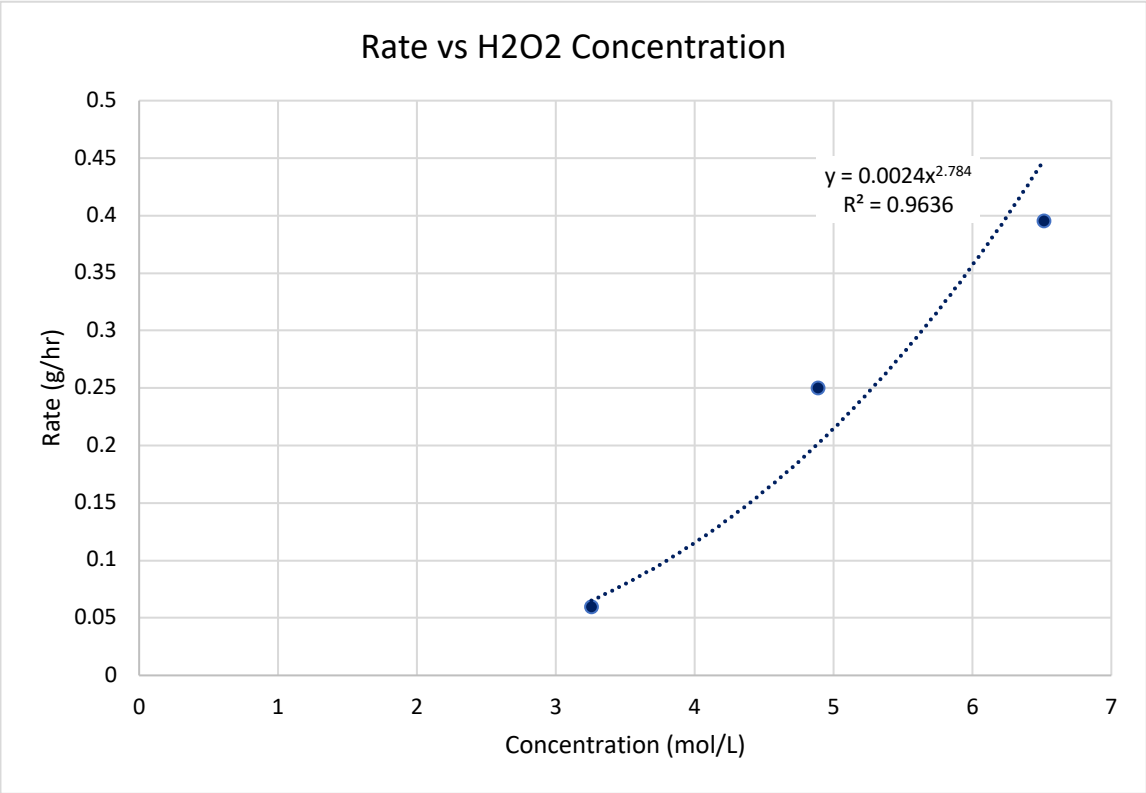

Fig. 5-8 Mass dissolution rate plotted against molar concentration, H_2O_2. Fit is modeled after concentration power relation.

Effects of Ethanol Concentration

The dependence of the reaction on concentration of ethanol was determined by mixing various volumes of ethanol with 10 mL hydrogen peroxide concentration, while adding deionized water to maintain a total volume of 30 mL. Figures 5-9, 5-10, and 5-11 plot changes in mass with time at various volumetric concentrations of 17%, 33%, and 50% ethanol. It can be seen that the rate of mass dissolution increases with increasing ethanol concentration, starting at 0.06 g/hr for 17% volumetric and ending at 0.283 g/hr for 50% volumetric. The rate at which epoxy dissolves increases less with ethanol concentration when compared to the rate increase with hydrogen peroxide concentration. This can be interpreted as adding more ethanol providing more molecules of solvent and ethanol/hydrogen peroxide radical products to react with the epoxy, though hydrogen peroxide is still necessary and more effective for removing the epoxy. Fitting a power function and comparing to the ethanol portion of the kinetic model in figure 5-12, the constant *c* can be calculated to be:

$$a * [EtOH]^c = 0.0138x^{1.357}$$

$$c = 1.357$$

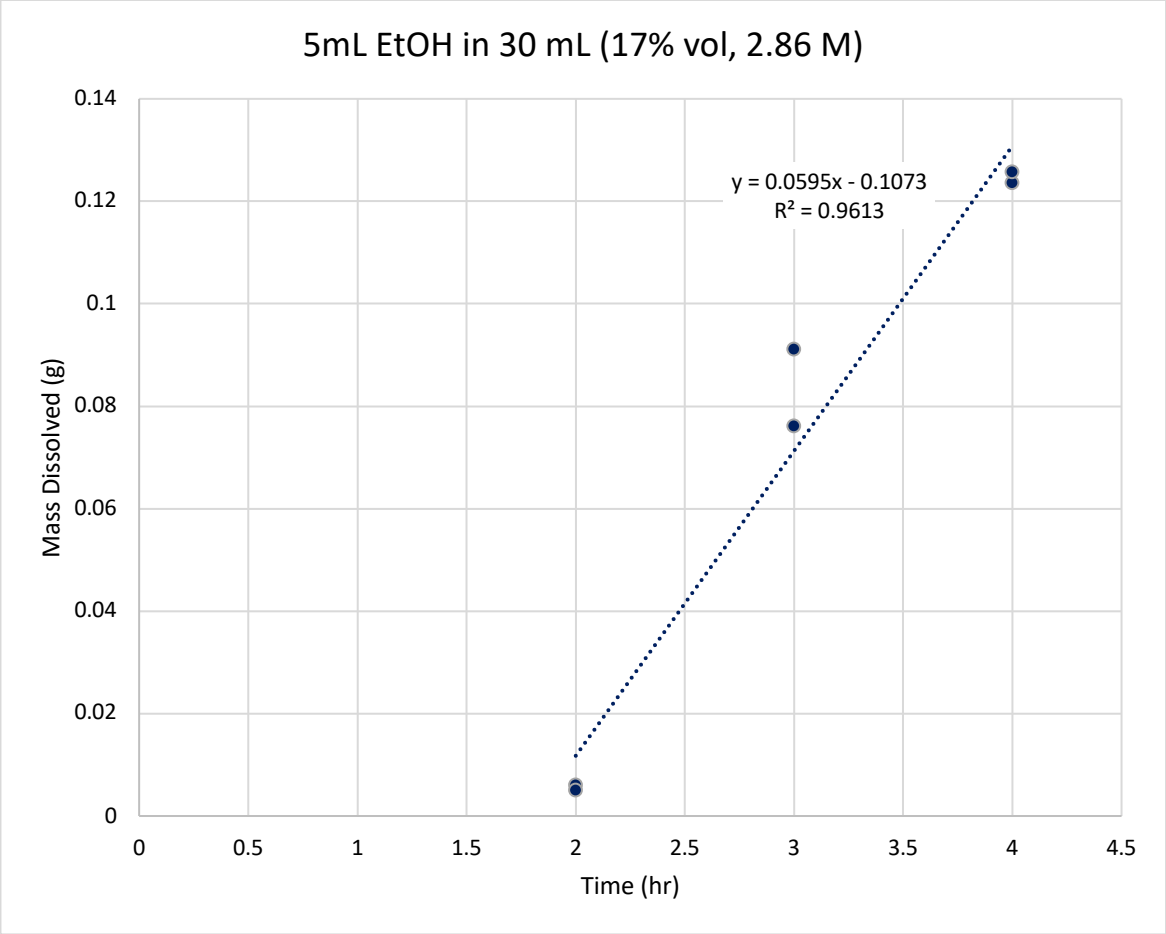

Fig. 5-9 Change in mass plotted over time, 17% vol EtOH. Estimated 0.0595 g dissolved per hour, with offset for heating to reaction temperature.

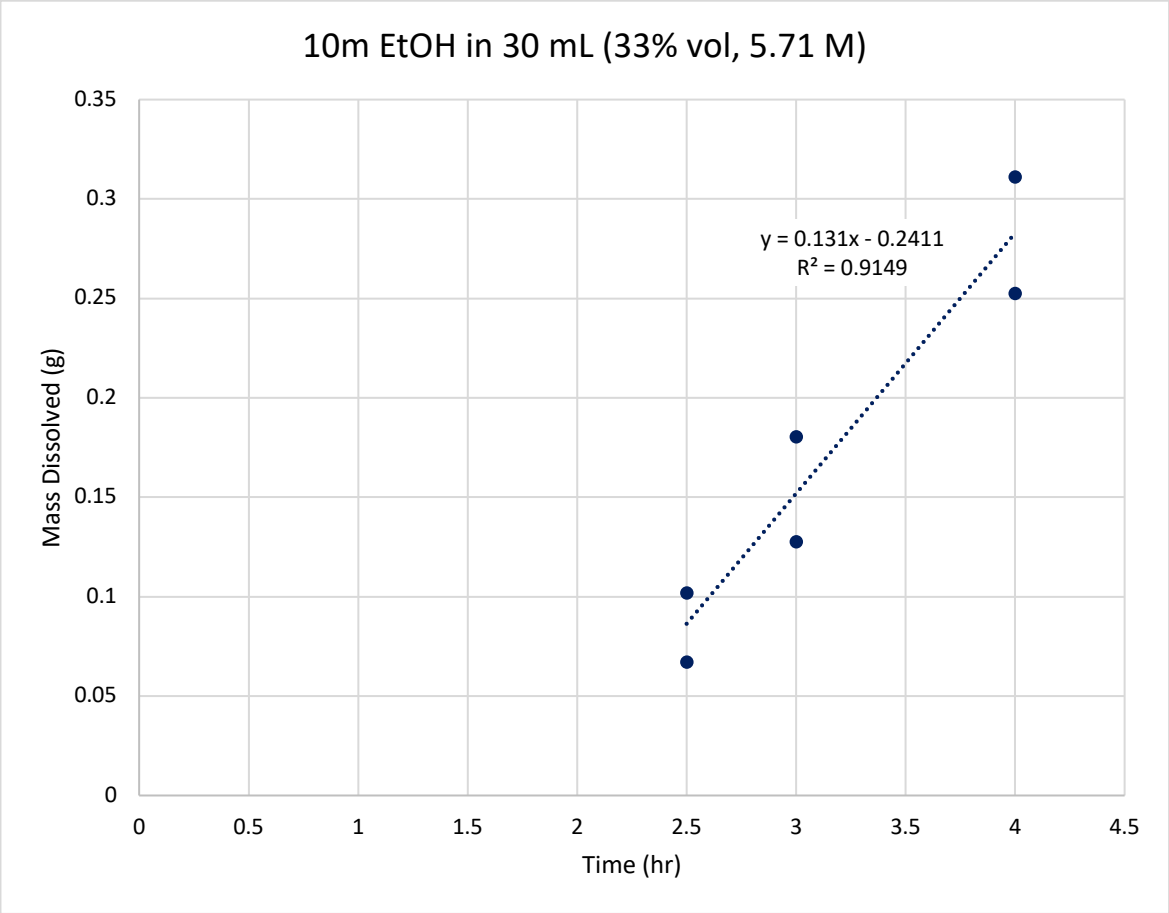

Fig. 5-10 Change in mass plotted over time, 33% vol EtOH. Estimated 0.131 g dissolved per hour, with offset for heating to reaction temperature.

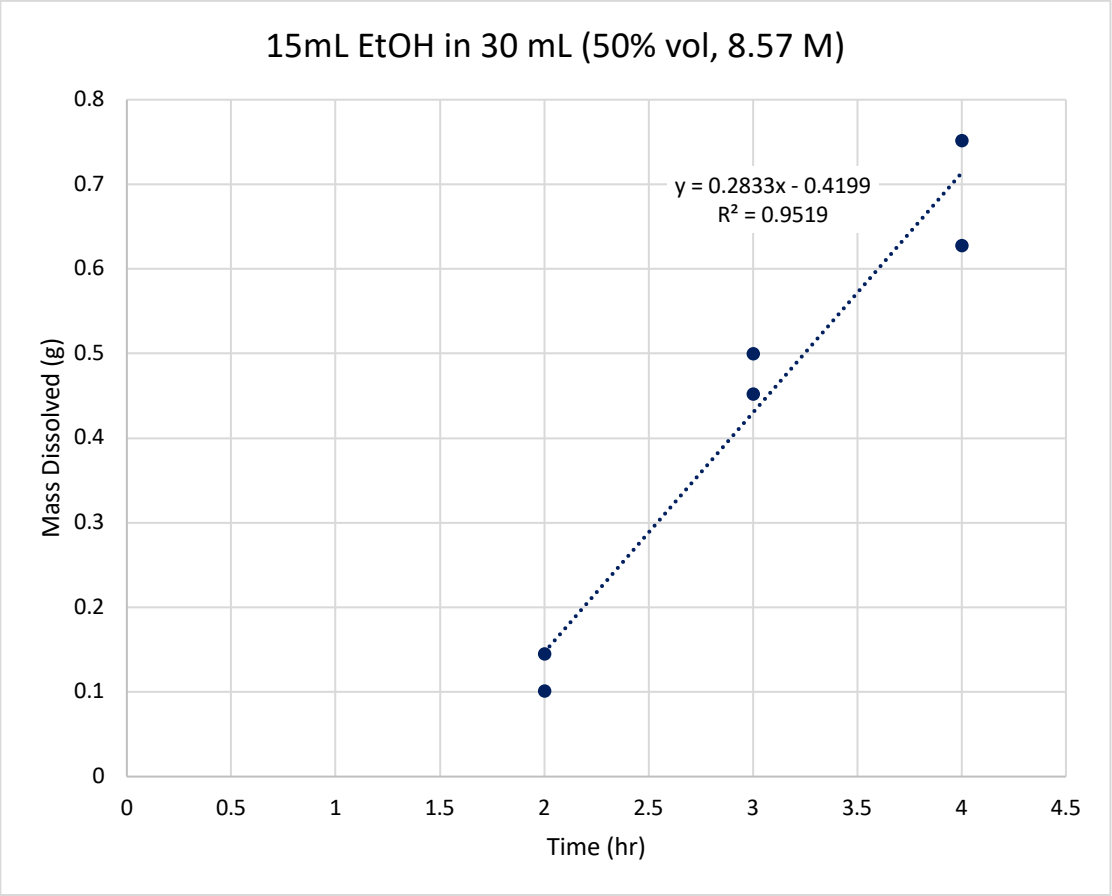

Fig. 5-11 Change in mass plotted over time, 50% vol EtOH. Estimated 0.2833 g dissolved per hour, with offset for heating to reaction temperature.

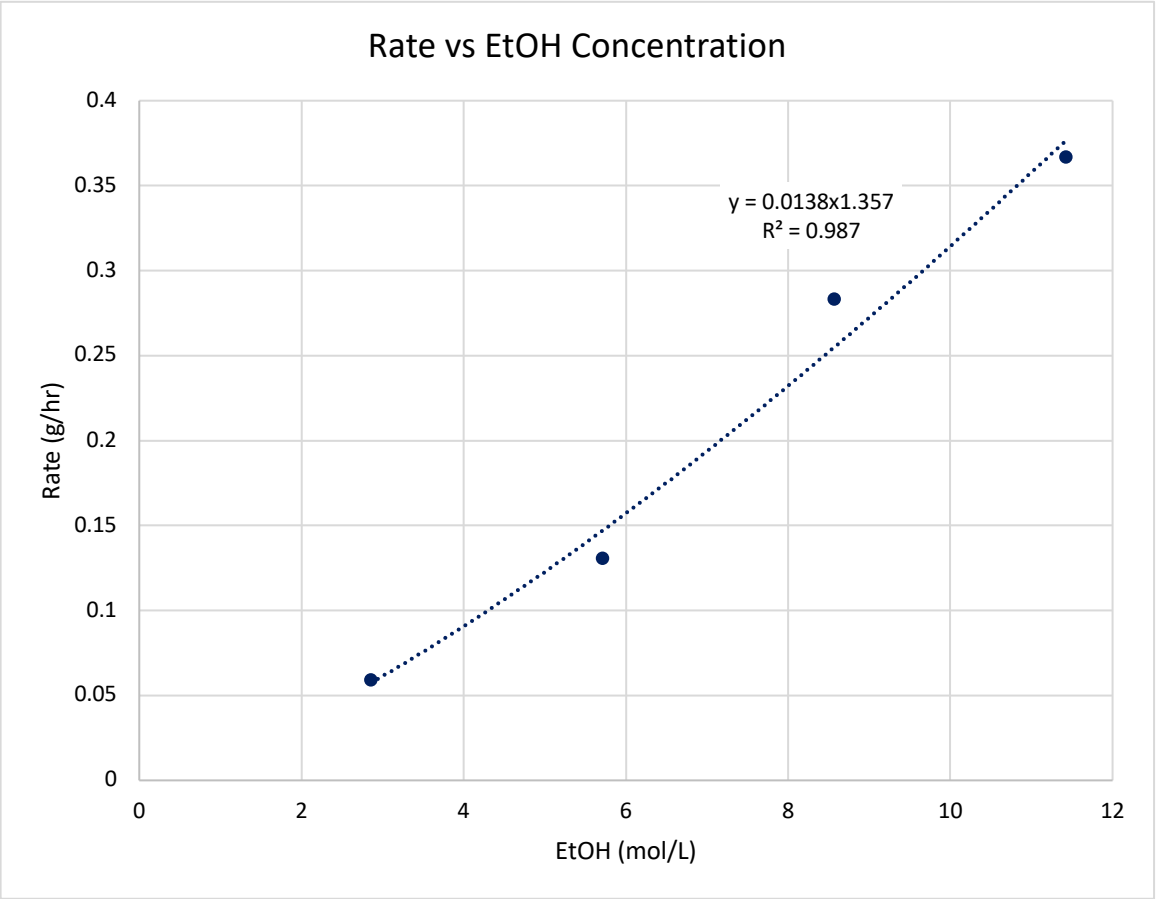

Fig. 5-12 Mass dissolution rate plotted against molar concentration, ethanol. Fit is modeled after concentration power relation.

Effects of Surface Area

The effects of surface area on the reaction was determined by plotting the rate of mass loss for varying surface areas. Figures 5-13, 5-14, and 5-15 are plots of mass dissolved over time for total exposed surface areas of 940 mm^2, 2900 mm^2, and 4280 mm^2. With increasing surface area, the rate at which epoxy is dissolved increases. This is due to the increasing availability of epoxy sites that the radicals can react with.

Figures 5-16 and 5-17 are graphs plotting mass dissolution rates over exposed surface areas. An initial fitting for the plot in figure 5-16 resulted in the linear equation of

$$y = 8 * 10^{-5}x + 0.1229$$

wherein x is the surface area (mm2). For this situation it could be reasoned that a y-intercept of 0 should be present, as no reaction should occur with no surface area in contact with solution. With the y-intercept set as 0 in figure 5-17, an equation of

$$y = 0.0001x$$

is calculated. This is similar to the first equation rate rounded upwards, and so the dependence of the mass loss rate on exposed surface area was determined to be 0.0001g/mm^2/hr.

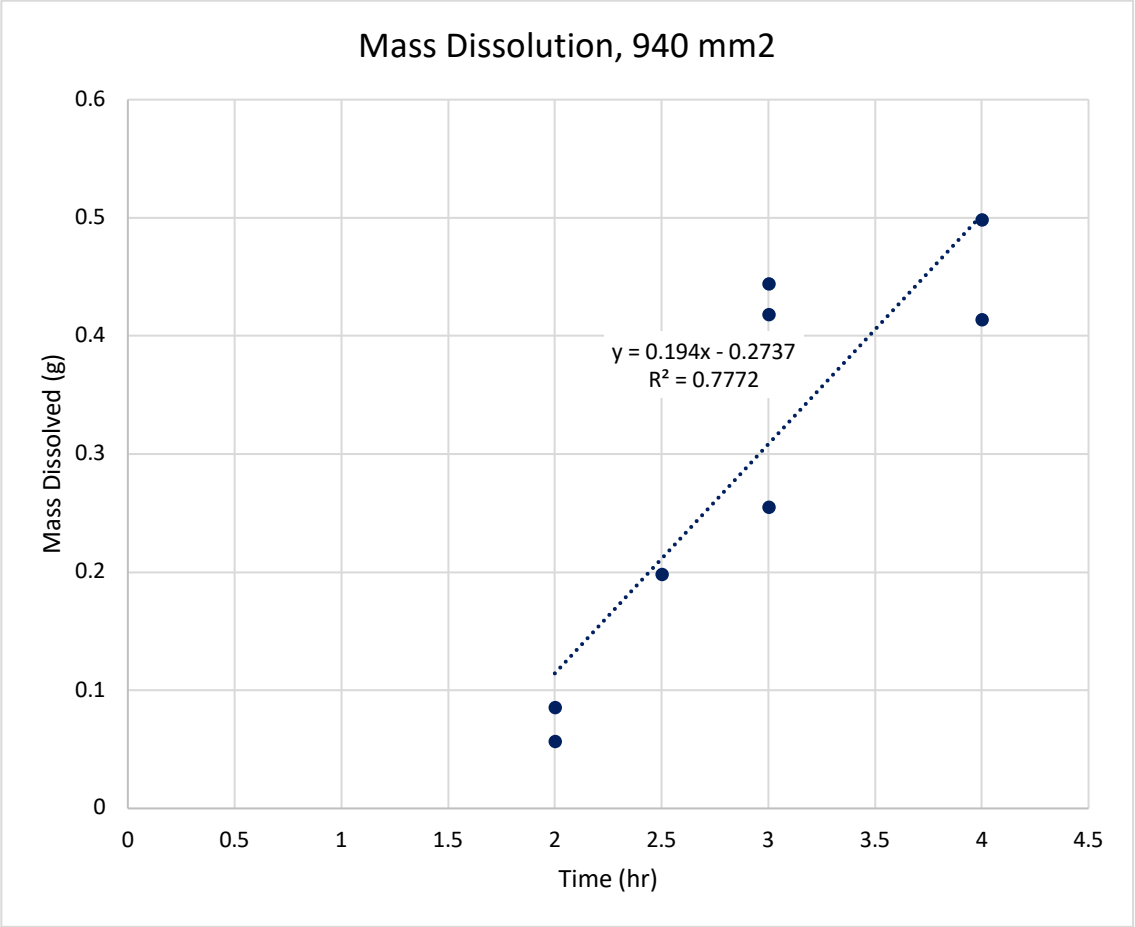

Fig. 5-13 Change in mass plotted against time, 940 mm^2 exposed. Estimated 0.194 g dissolved per hour, with offset for heating to reaction temperature.

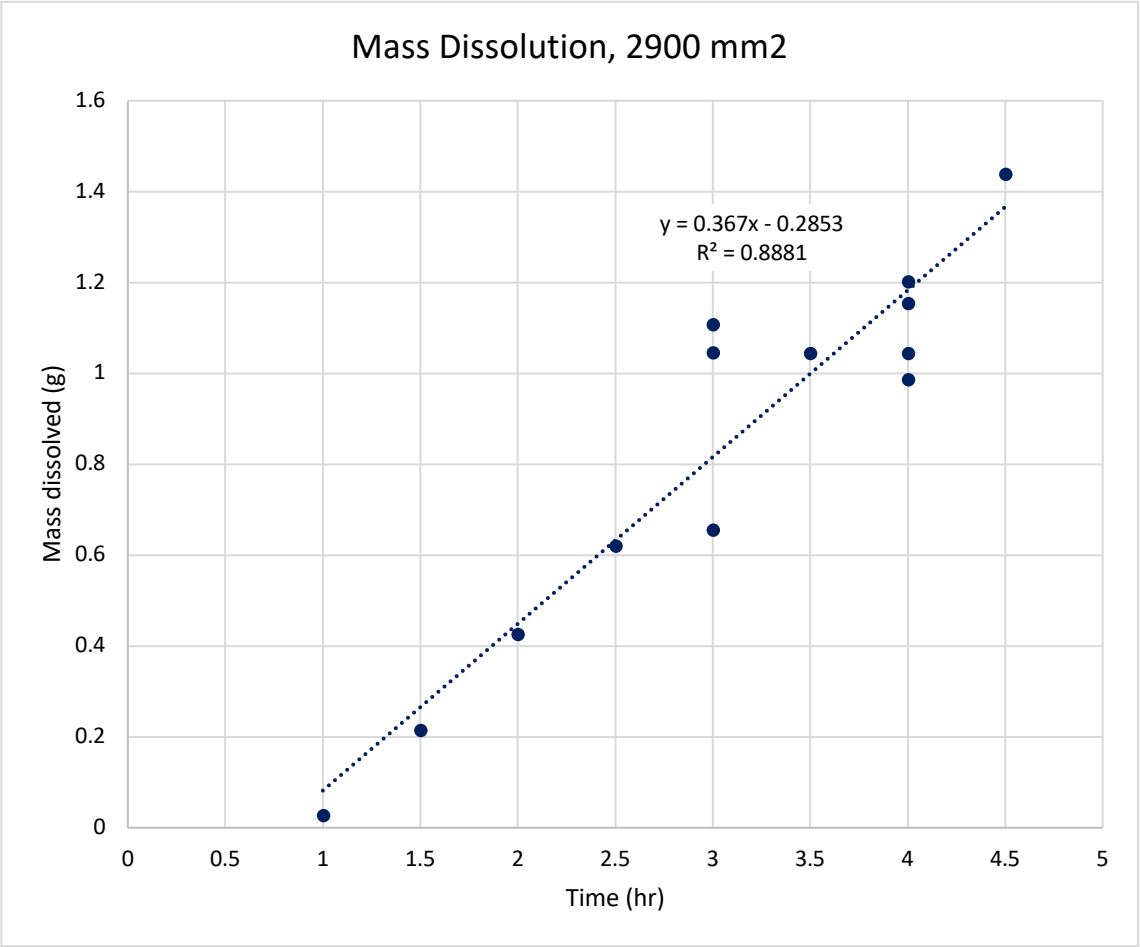

Fig. 5-14 Change in mass plotted against time, 2900 mm^2 exposed. Estimated 0.367 g dissolved per hour, with offset for heating to reaction temperature.

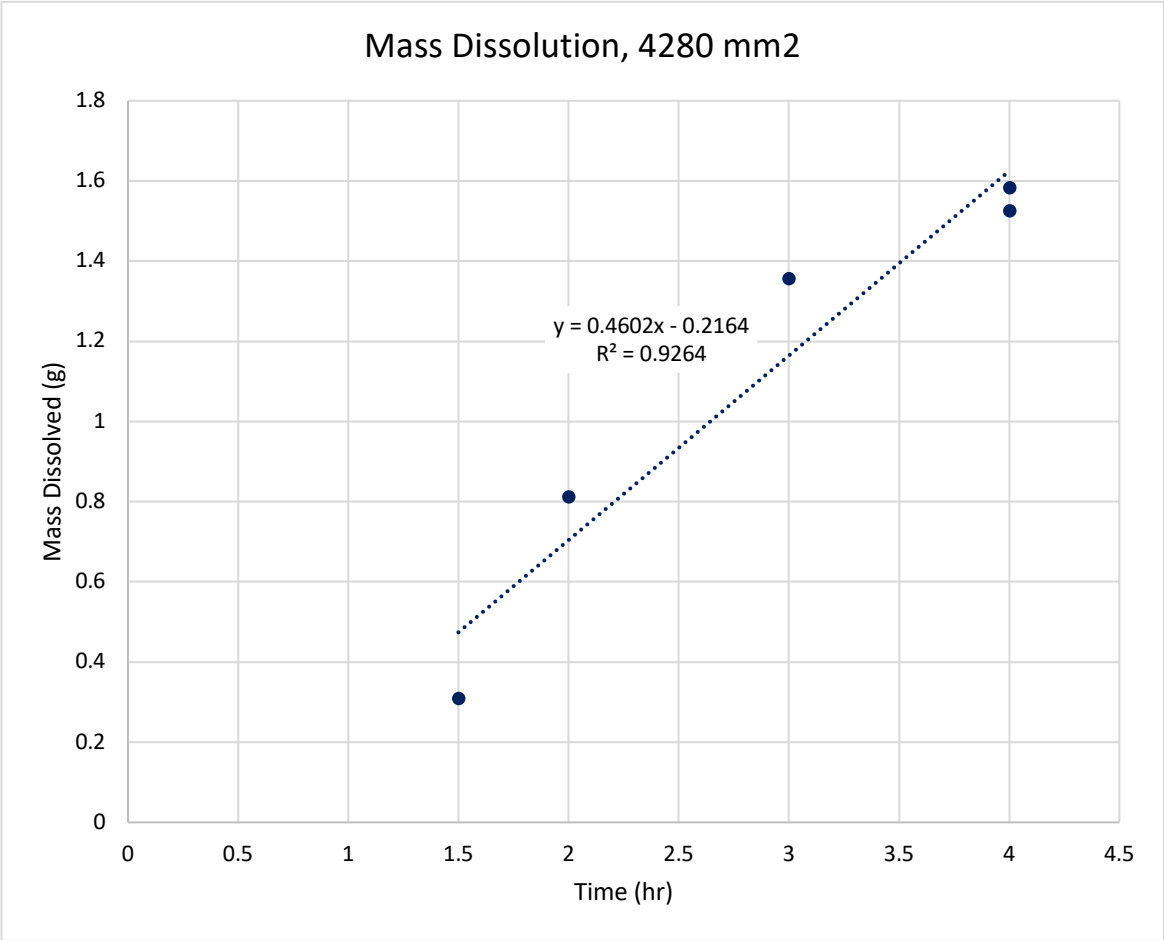

Fig. 5-15 Change in mass plotted against time, 4280 mm^2 exposed. Estimated 0.460 g dissolved per hour, with offset for heating to reaction temperature.

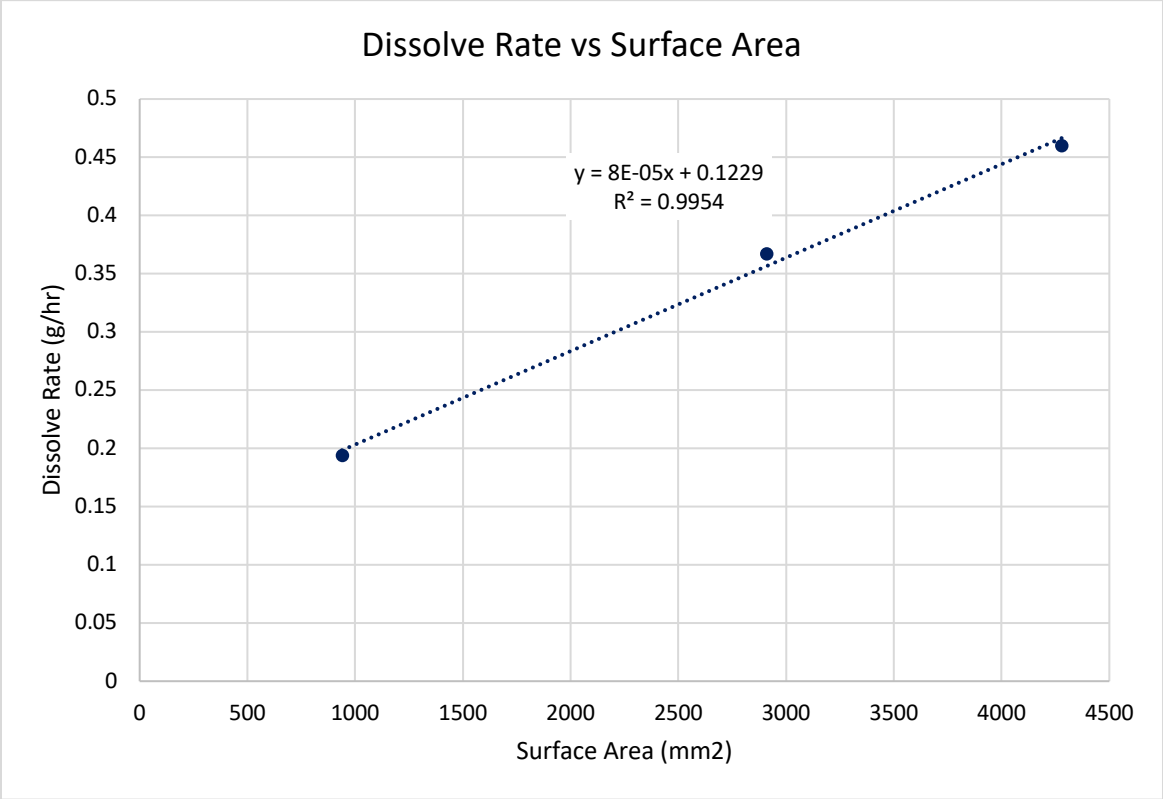

Fig. 5-16 Mass dissolve rate plotted against exposed surface area with nonzero y-intercept

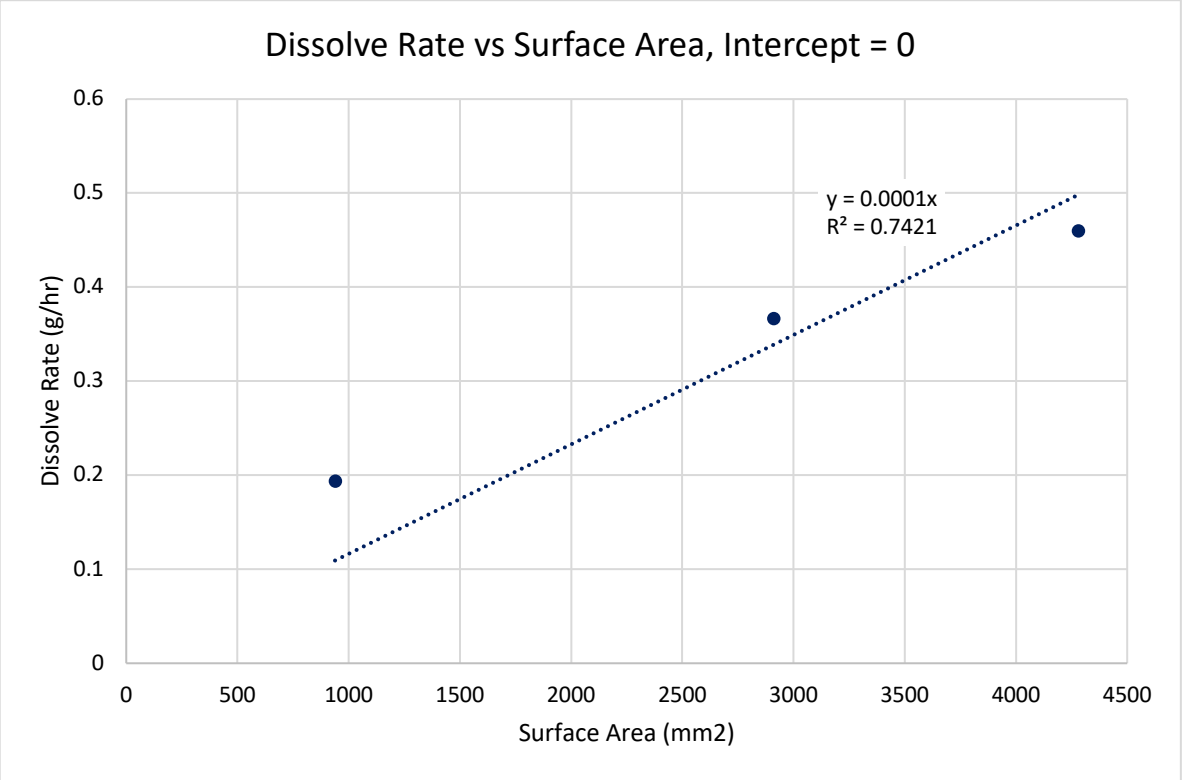

Fig. 5-17 Mass dissolve rate plotted against exposed surface area with y-intercept = 0

Fitting the Model

After calculating the variables associated for temperature, concentrations, and exposed surface area the model appears as

$$\frac{dM}{dt} = a * \exp\left(-\frac{-44812.46}{RT}\right) * [H_2O_2]^{2.785} * [EtOH]^{1.357} * 0.0001 * SA$$

Experimental data was fit into this model in order to calculate the final variable *a*, leading to a final model of

$$\frac{dM}{dt} = 0.155 * \exp\left(-\frac{-44812.46}{RT}\right) * [H_2O_2]^{2.785} * [EtOH]^{1.357} * SA$$

Where R is in units of J/mol/K, concentrations are in units of *M* (mol/L), surface area (SA) is in units of mm^2, and mass loss rate dM/dt is in units of g/hr.

Validation of the Model

The model was used to predict the mass lost for each of the experiments run and compared to the experimental data. The average percent errors for each temperature can be found in table 5-1 and range between 6.1% and 7.6%, implying that the kinetic model correlates very well with the reaction parameters. For a specific case study, a 4.5g composite sample was considered. Given that the mass composition of the composites was determined by TGA to be 28% epoxy and 72% carbon fiber (found in figure 5-18), it was estimated that 1.26g of epoxy needed to be removed. Running the sample through a process of 150°C in 10 mL hydrogen peroxide solution and 20 mL ethanol with 2900 mm^2 exposed to the solution, the kinetic model predicted a mass loss rate of 0.97 g/hr. Considering the time required for the reactants and chamber vessel to preheat, the linear equation for mass loss was determined to be

$$1.26 = 0.97t - 0.2934$$

$$t \approx 1.6 \text{ hr}$$

A similar sample that was run through the same process for 1.5 hours was found to have almost all epoxy removed, further proving good correlation between the kinetic model and the reaction. Figure 5-19 is an image of the sample.

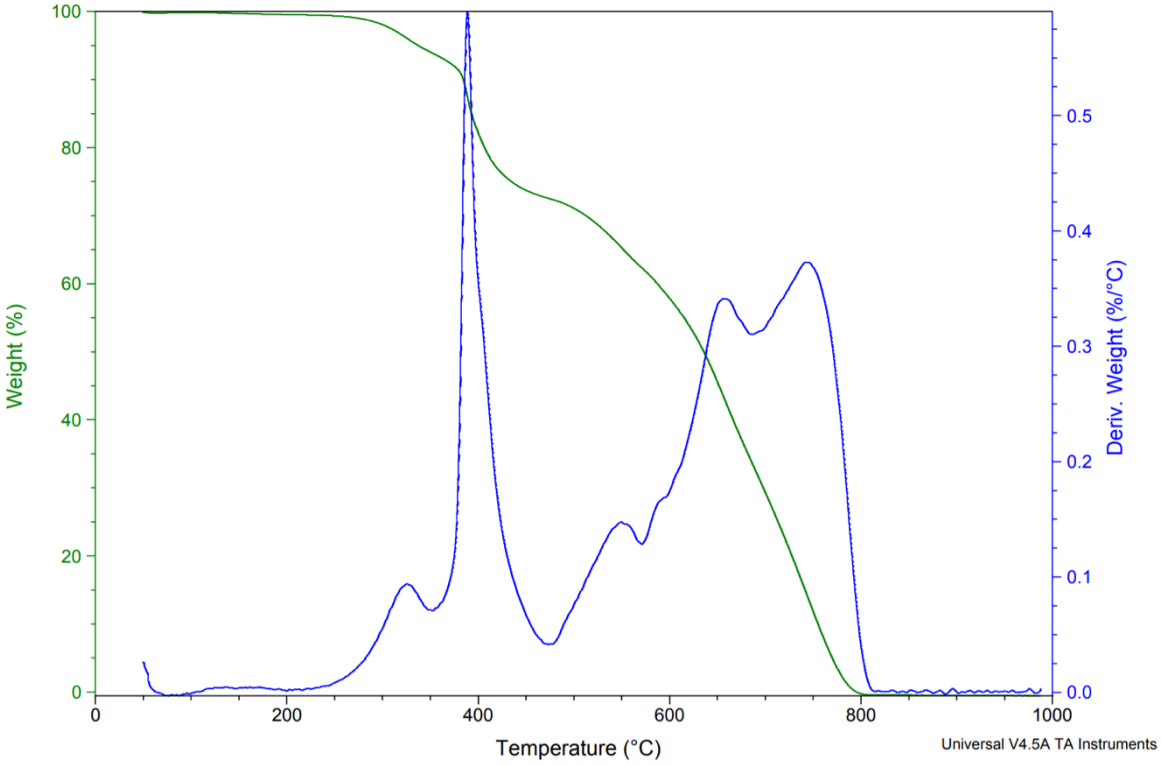

Fig. 5-18 TGA analysis of CFRP for mass composition

Temperature (°C)	Average % Error
120	6.6
130	6.4
140	6.1
150	7.6

Table 5-1 Percent error between kinetic model and experimental data

Fig. 5-19 CFRP processed for 1.5 hours at 150°C. The majority of the fibers were either released or could be easily removed from the sample

Conclusion

In this section, a kinetic model was developed for the hydrogen peroxide/ethanol solution. The parameters considered included temperature, hydrogen peroxide concentration, ethanol concentration, and exposed surface area. Changes in mass over time was measured for each parameter and linear relations were graphed in scatterplots and commonly known kinetic equations were fitted in order to determine the constants related to each parameter. The kinetic model was then compared to experimental data to determine the final constant. This final model was then used to calculate theoretical mass loss for each experiment conducted and was compared to experimental data. Errors were found to be low percentage, indicating good correlation. Thus, the kinetic model equation determined in this section can be used to predict optimal reaction parameters to maximize epoxy removal and carbon fiber recovery.

Chapter 6 Comparison to Using Sulfuric Acid and Other Recycling Approaches

Introduction

Highly concentrated sulfuric acid is an alternative solution used to decompose the epoxy and recover fibers from CFRP. In particular one of the common standard methods to determine fiber content of CFRP is to dissolve the epoxy in fuming sulfuric acid[39]. After dissolving the solution becomes dark brown. This change is attributed to the removal of binder and carbon fiber dust deposited during fiber fabrication and processing. This dark brown solution requires the addition of hydrogen peroxide solution to become clear. The fibers can then be easily filtered and removed from the solution. Even though hydrogen peroxide is still used it is important to analyze the performance of highly concentrated sulfuric acid in epoxy dissolution and fiber strength retention.

Mass Loss Comparison

Dissolution in sulfuric acid is another possible method to dissolve the epoxy and recover carbon fibers from composites. In this work composite samples were left in 30 mL of 99% sulfuric acid at 120°C. Results from these experiments were compared to the results for composites processed in hydrogen peroxide/ethanol at the same temperature of 120°C.

The mass loss rate for the sample in hydrogen peroxide/ethanol solution was found to be larger compared to the rate for sulfuric acid. Figure 6-1 shows that the rate at which mass was lost was 0.208 g/hr for sulfuric acid, compared to figure 6-2 which shows a rate of 0.367 g/hr for hydrogen peroxide/ethanol at the same temperature. This rate is higher by 0.159 g/hr, or higher by 76%. The conclusion to be taken from these results is that the oxidation caused by the hydrogen peroxide/ethanol solution removes epoxy faster than the acidic dissolution caused by sulfuric acid.

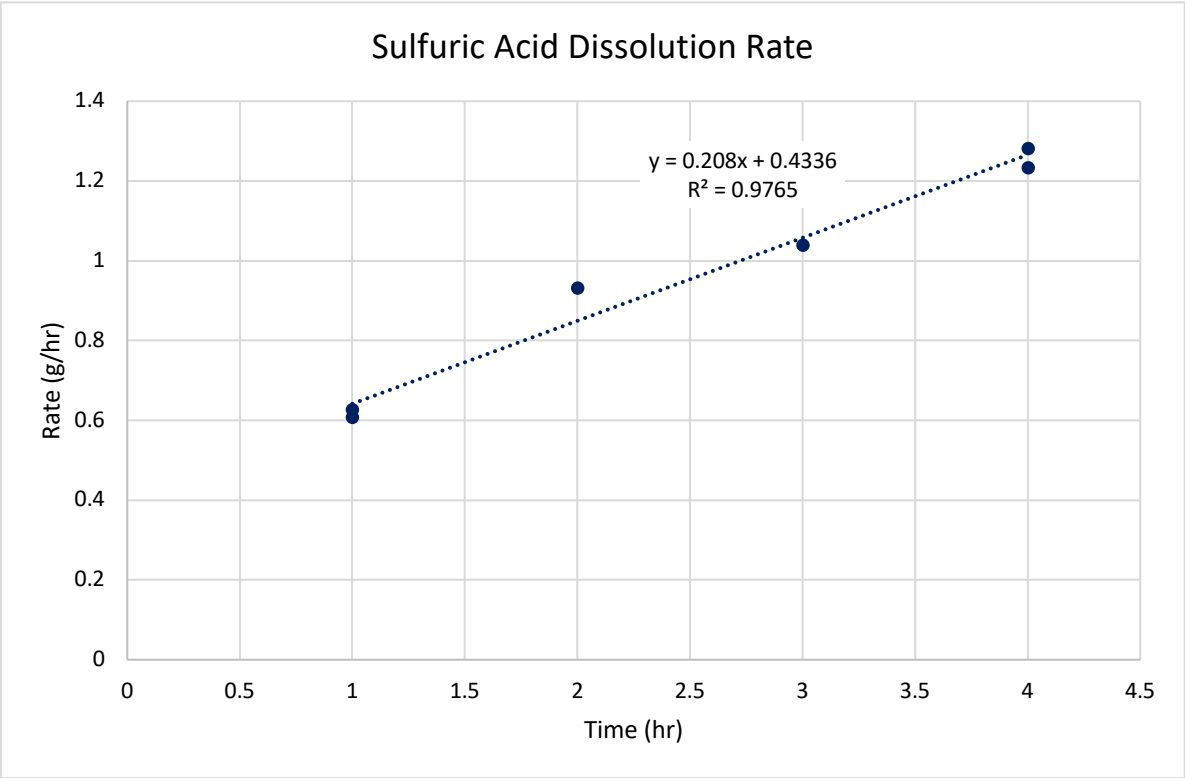

Fig. 6-1 Mass dissolved over time for samples process in sulfuric acid. Estimated 0.208 g dissolved per hour, with offset for heating to reaction temperature.

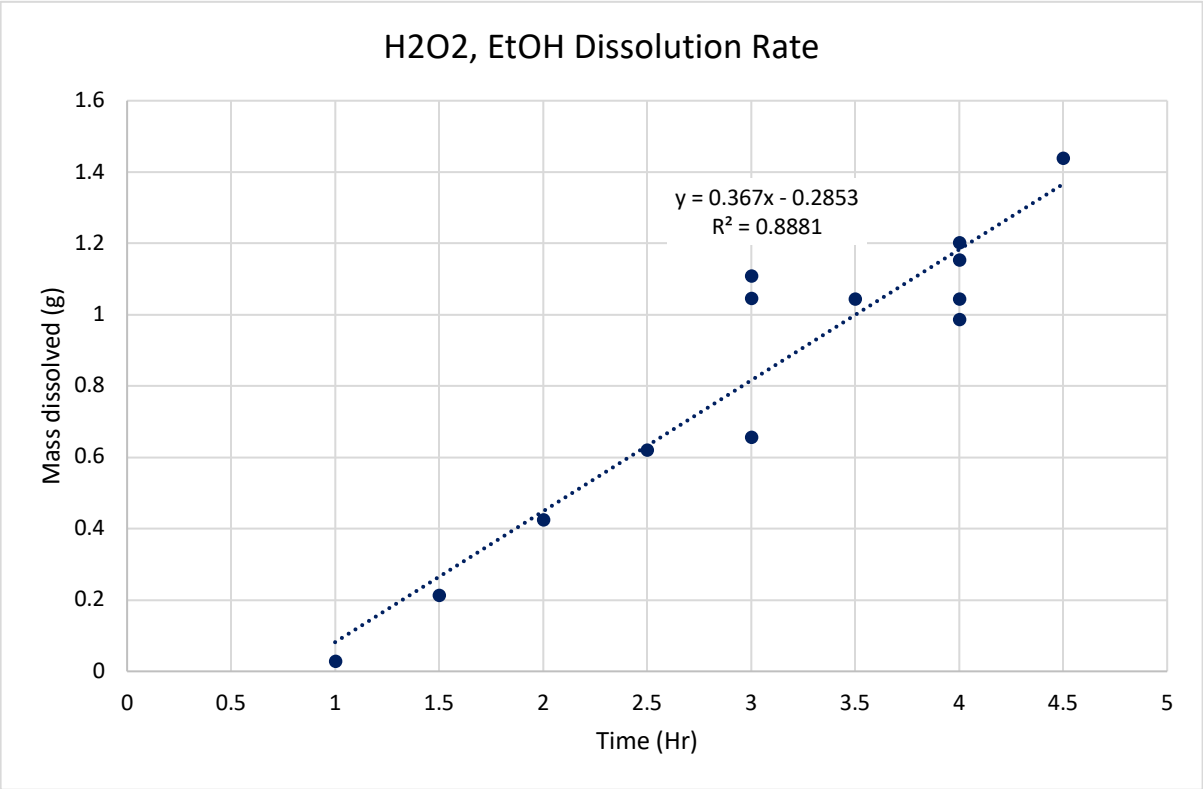

Fig. 6-2 Mass dissolved over time for samples processed in hydrogen peroxide and ethanol. Estimated 0.367 g dissolved per hour, with offset present for heating to reaction temperature.

Figures 6-3 and 6-4 are SEM images taken of the fibers recovered from the sulfuric acid process and fibers recovered using hydrogen peroxide/ethanol. The fibers in both images look similar with no visible damage and no notable differences. The conclusion is that neither process fundamentally changes the fibers.

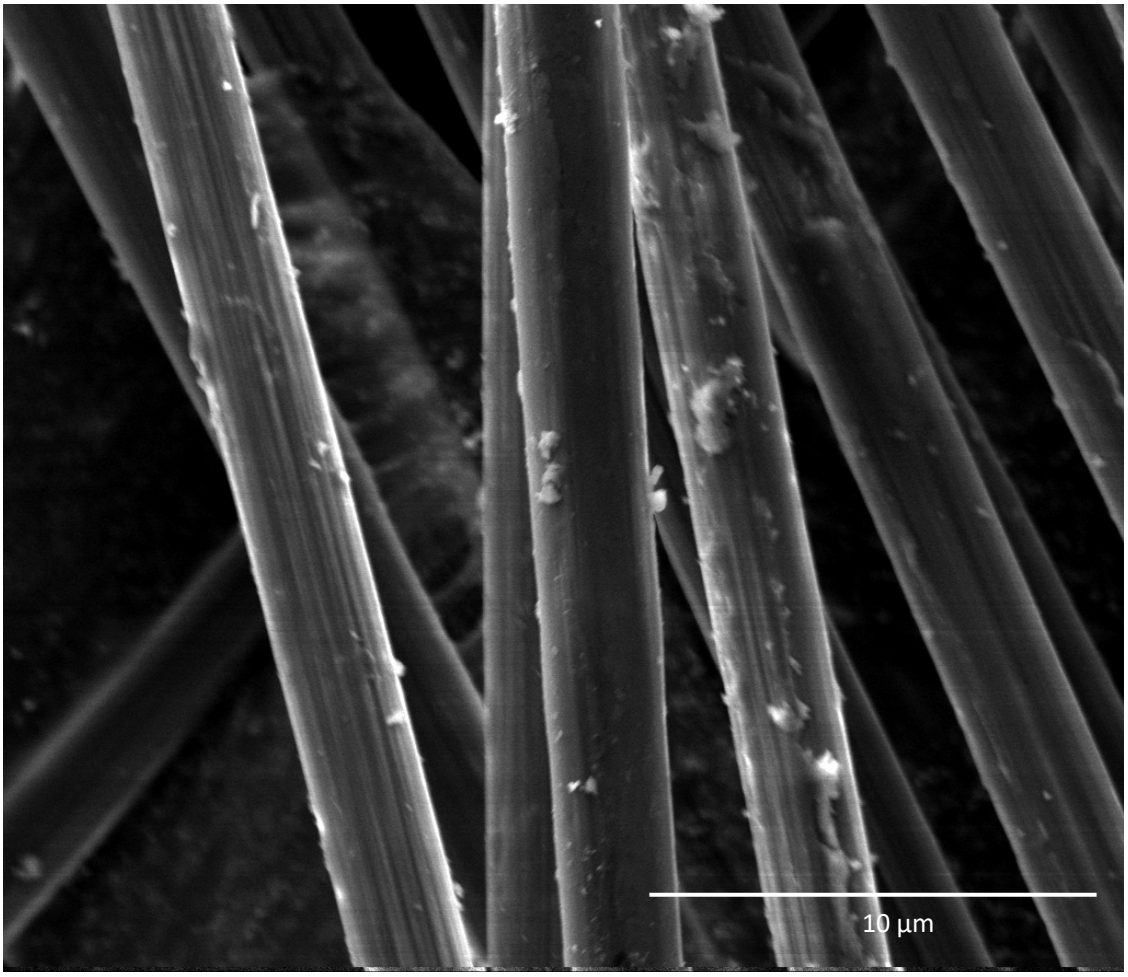

Fig. 6-3 Fibers recovered using H_2O_2 and EtOH.

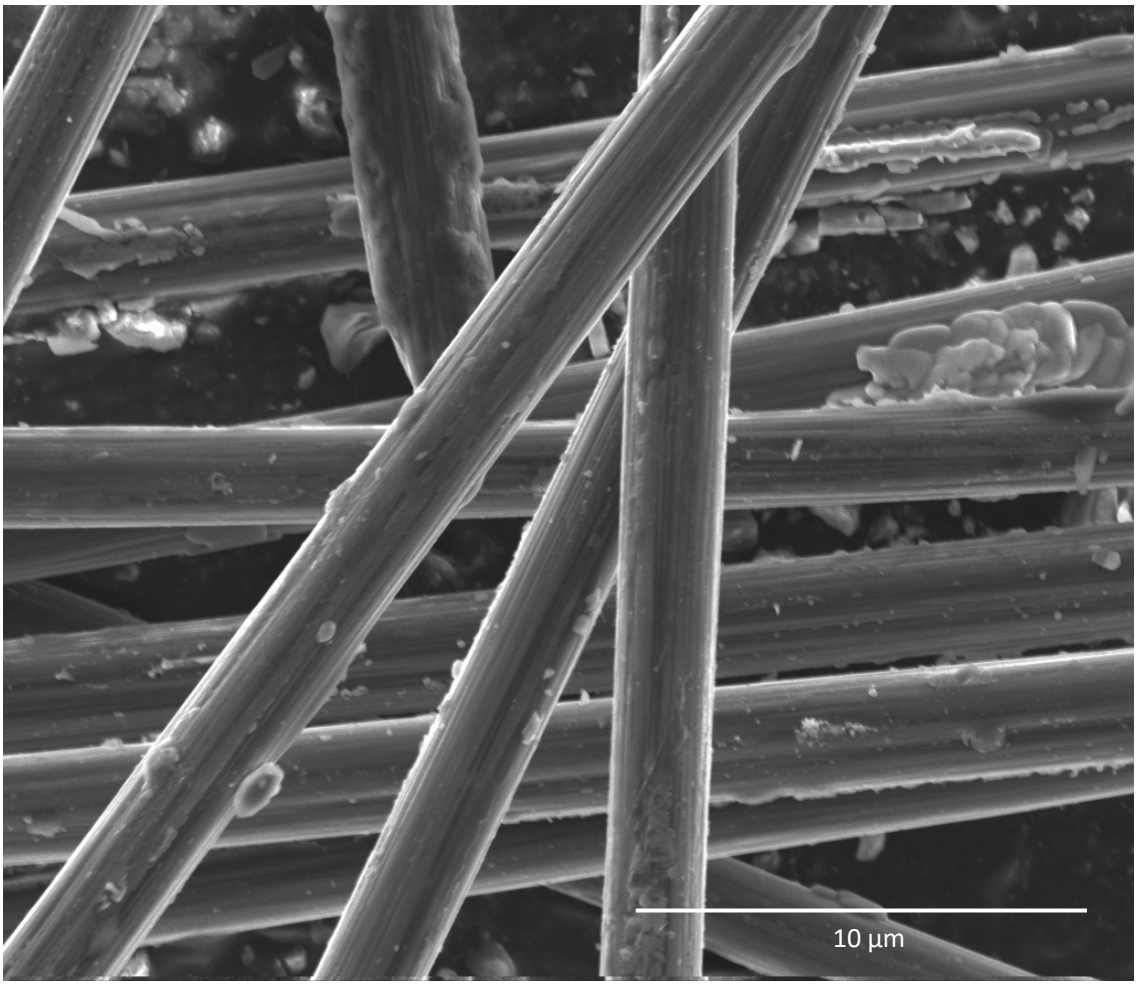

Fig. 6-4 Comparison of fibers recovered using sulfuric acid.

Fiber Strength Comparison

The tensile strength for fibers recovered from samples processed in hydrogen peroxide/ethanol and sulfuric acid for 4 hours were tested and compared. Figure 6-5 shows the stress strain curves of the fibers recovered from sulfuric acid with the average tensile stress. Figure 6-6 shows the stress strain curves of the fibers recovered from the hydrogen peroxide/ethanol solution under the same amount of time. Measured and calculated average values for control (virgin) samples and samples processed using both methods can be found in table 6-1. The results from these measurements seem to indicate that the fibers recovered using sulfuric acid are stronger in tensile strength. However, it should be noted that samples processed at the same time will not be similar due to the difference in fiber recovery performance. As such another comparison was made between samples with similar amounts of epoxy removed.

The amount of epoxy dissolved from a sample processed in sulfuric acid for 4 hours was equivalent to the epoxy dissolved from a sample processed in the hydrogen peroxide/ethanol solution for 2.5 hours. Figure 6-7 shows the stress-strain curves and average tensile strength for these fiber samples. Table 6-2 again lists the measured and calculated average values for virgin samples and processed samples. They are stronger than those processed by 4 hours by about 4%, making them weaker than the fibers processed in sulfuric acid by only. about 4%. It could thus be concluded that the fiber strength in both processes are similar, and also that fiber strength is ultimately dependent on how long the fibers have been exposed to the dissolving solution.

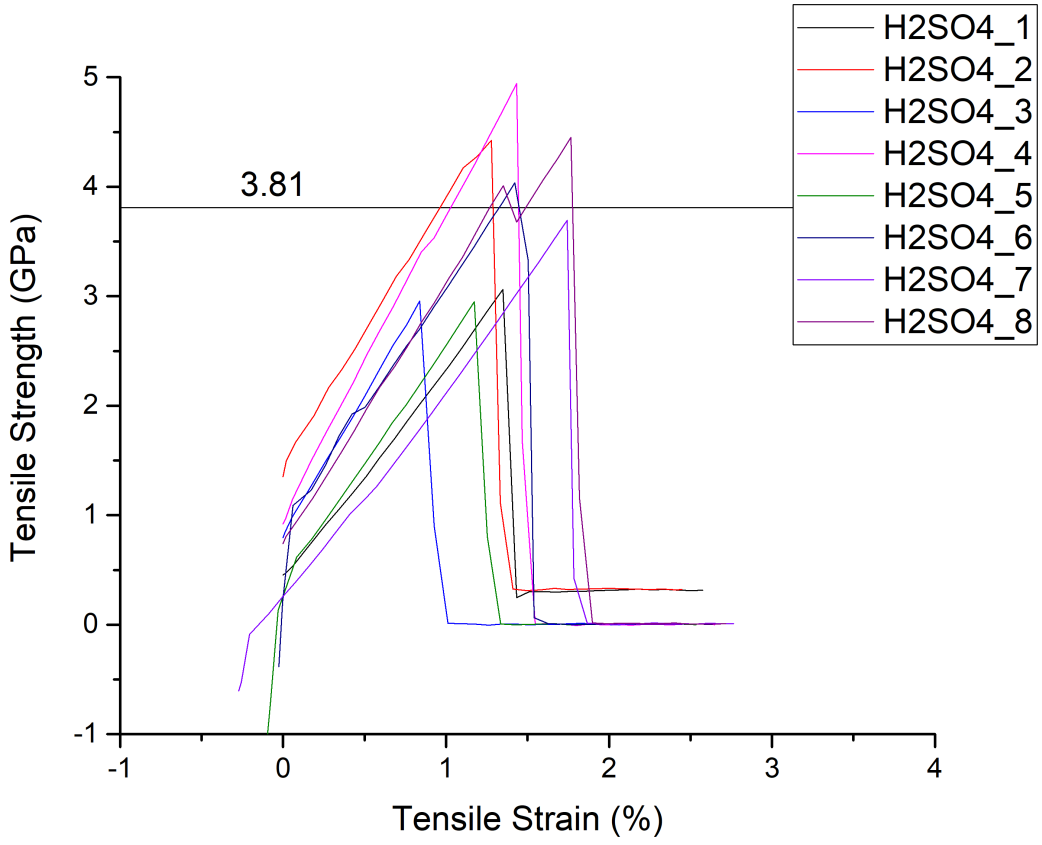

Fig. 6-5 Tensile strength of fibers recovered using sulfuric acid for 4 hours. Average strength is 3.81 GPa.

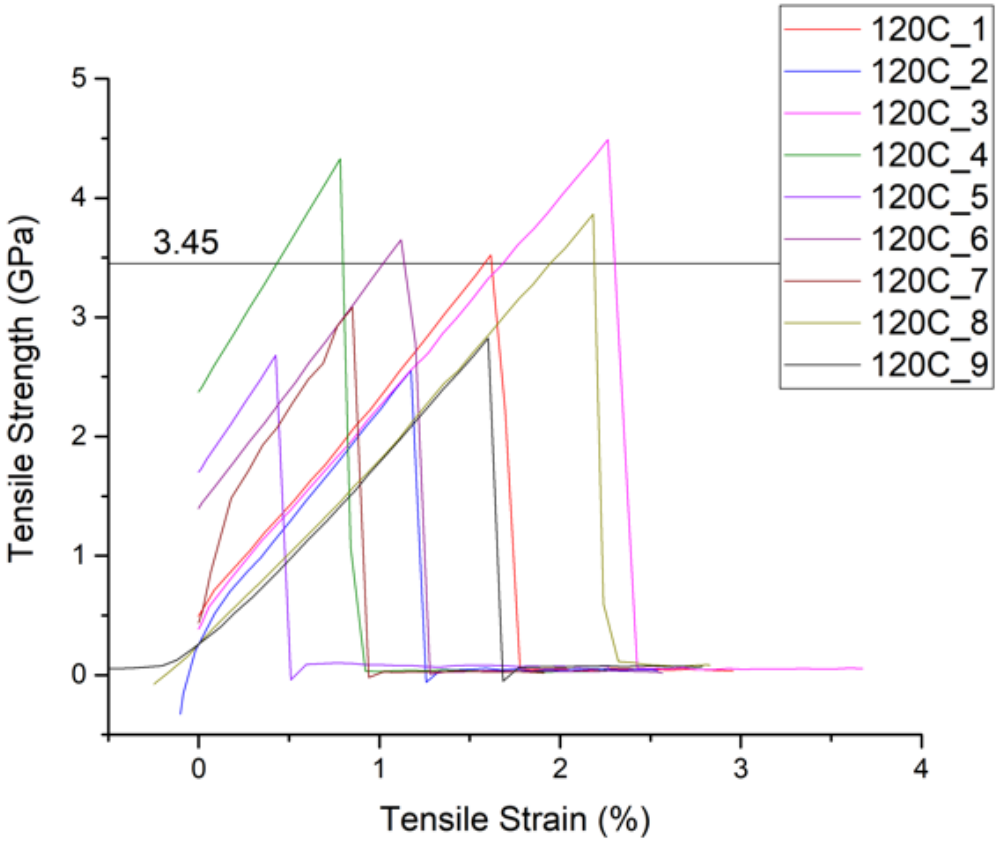

Fig. 6-6 Tensile strength of fibers recovered using H_2O_2 and EtOH for 4 hours. Average strength is 3.45 GPa.

Fiber	Strength (Gpa)	% Change	Weibull
Control	4.11(±0.38)	0	9.64
H_2O_2 + EtOH	3.45(±0.51)	16	3.33
H_2SO_4	3.81(±0.77)	7.3	5.50

Table 6-1: Tensile strength comparison between virgin fibers (control), fibers processed using H_2O_2/ethanol, and fibers processed using sulfuric acid. Samples were processed for the same amount of time

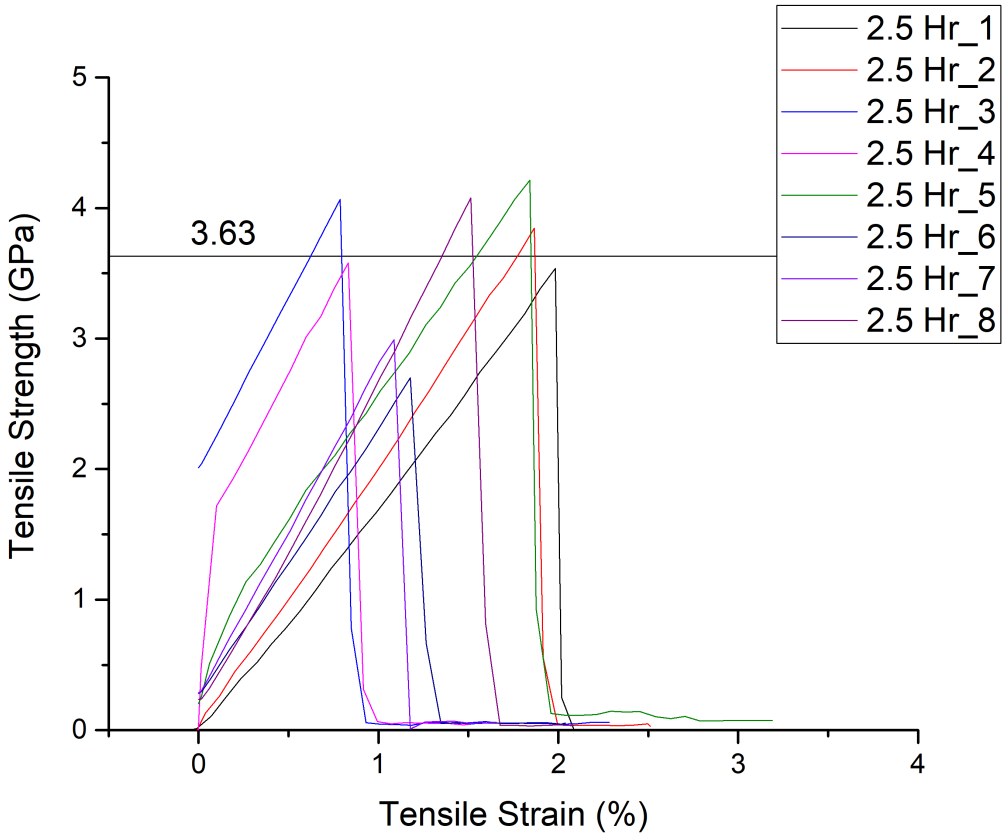

Fig. 6-7 Tensile strength of fibers recovered using H_2O_2 and EtOH for 2.5 hours. Average strength is 3.63 GPa.

Fiber	Strength (Gpa)	% Change	Weibull
Control	4.11(±0.38)	0	9.64
H_2O_2 + EtOH	3.63(±0.54)	11.7	7.43
H_2SO_4	3.81(±0.77)	7.3	5.50

Table 6-2: Tensile strength comparison between virgin fibers (control), fibers processed using H_2O_2/ethanol, and fibers processed using sulfuric acid. Samples were processed for the same fiber recovery performance

Overall the hydrogen peroxide/ethanol solvolysis method presented here appears to be the best option when compared to the other existing methods. Table 6-3 presents the alternative methods previously explored and compares them to the hydrogen peroxide/ethanol solvolysis method in terms of both operating conditions as well as the quality of the recovered fibers.

Alternative Method	**Comparison to H_2O_2 and Ethanol – Operations**	**Comparison to H_2O_2 and Ethanol – Recovered Fiber Quality**
Sulfuric Acid	Lower rate, larger safety concerns (100% H_2SO_4 vs 30% H_2O_2 in H_2O)	Similar Fiber Strength
Supercritical Alcohols	Much higher temperatures and pressures required	Stronger Fibers (2% vs 11% - 18% reduction)
Pyrolysis or Fluidized Bed	Very high temperatures, complicated equipment for fluidized bed	Weaker Fibers (5% - 30% vs 11% - 18%)
Mechanical	No need for heat or pressure	Complete loss of strength (fibers are ground into powder or small pieces)
Chemical	Similar temperature and pressure, but larger safety concerns (explosive byproducts)	Similar Fiber Strength

Table 6-3: Comparison of existing recycling methods to the hydrogen peroxide/ethanol solvolysis method. The hydrogen peroxide solvolysis method presents the best combination of operating conditions and quality of recovered carbon fibers.

Conclusion

In this section carbon fibers recovered from samples processed in hydrogen peroxide/ethanol were compared to fibers recovered from samples processed in sulfuric acid. It was found that composites exposed to the hydrogen peroxide/ethanol solution had mass removed at a faster rate, and fibers recovered from samples with similar fiber recovery performance had similar strength retention. These results indicate that using the hydrogen peroxide/ethanol solvolysis method presented in this work is more effective than using sulfuric acid, and that strength retention of the fibers depends on how long they are exposed to the dissolving solution.

Chapter 7 Effects of Incorporating Fenton Reagent to Hydrogen Peroxide and Ethanol on Epoxy

Introduction

The Fenton reaction is a process in which catalyst is used to create hydroxyl radicals from hydrogen peroxide. In the presence of a catalyst such as iron oxide (Fe^{2+}/Fe^{3+}), hydrogen peroxide will react in the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\cdot + HOO\cdot + H^+$$

Due to the involvement of a catalyst, the temperature required for reaction is greatly reduced. Thus, there is a strong potential to increase the energy efficiency of the hydrogen peroxide/ethanol reaction proposed in this work by using the Fenton reaction to create hydroxyl radicals rather than just using heat. However, at a pH level above 3.0, $Fe(OH)_3$ precipitates form, resulting in the reduction of ferric ions present to catalytically form hydroxyl radicals. Thus, the solution must be maintained at an acidic pH.

For the experiments in this work, the catalyst used is 8 mg iron sulfate heptahydrate dissolved in 1 mL H_2O. This was mixed with ~0.5 mL sulfuric acid to maintain a low pH level (pH~3). 10 mL hydrogen peroxide and 20 mL ethanol were added for the standard oxidizing solution. The sample and solution were placed in the autoclave vessel in the oven at 80°C for between 1 and 3 hours.

Results and Discussion

Based on initial results, it appears that epoxy can be successfully removed from composites at significantly lower temperatures. Figure 7-1 is a plot of change in mass over time for experiments conducted using the Fenton reaction. At 80°C the average mass removal rate was 0.185 g/hr, a little more than half of the rate determined at 120°C. Although the correlation R^2 is low, the rate at which mass dissolved increases with time appears to be consistent between points. Additional experiments with the same conditions would improve the R^2. Nevertheless, it is ultimately clear that the use of a Fenton reagent significantly lowers the temperature necessary for the oxidizing radicals to react with and decompose the epoxy.

Additional experiments using 5 mL hydrogen peroxide/25 mL ethanol found some mass removed (0.02g – 0.03g). These results indicate that by using ferrous ions in acidic solution the reaction utilized in this work can be operated at lower temperatures and concentrations, which would further lower the cost of operations.

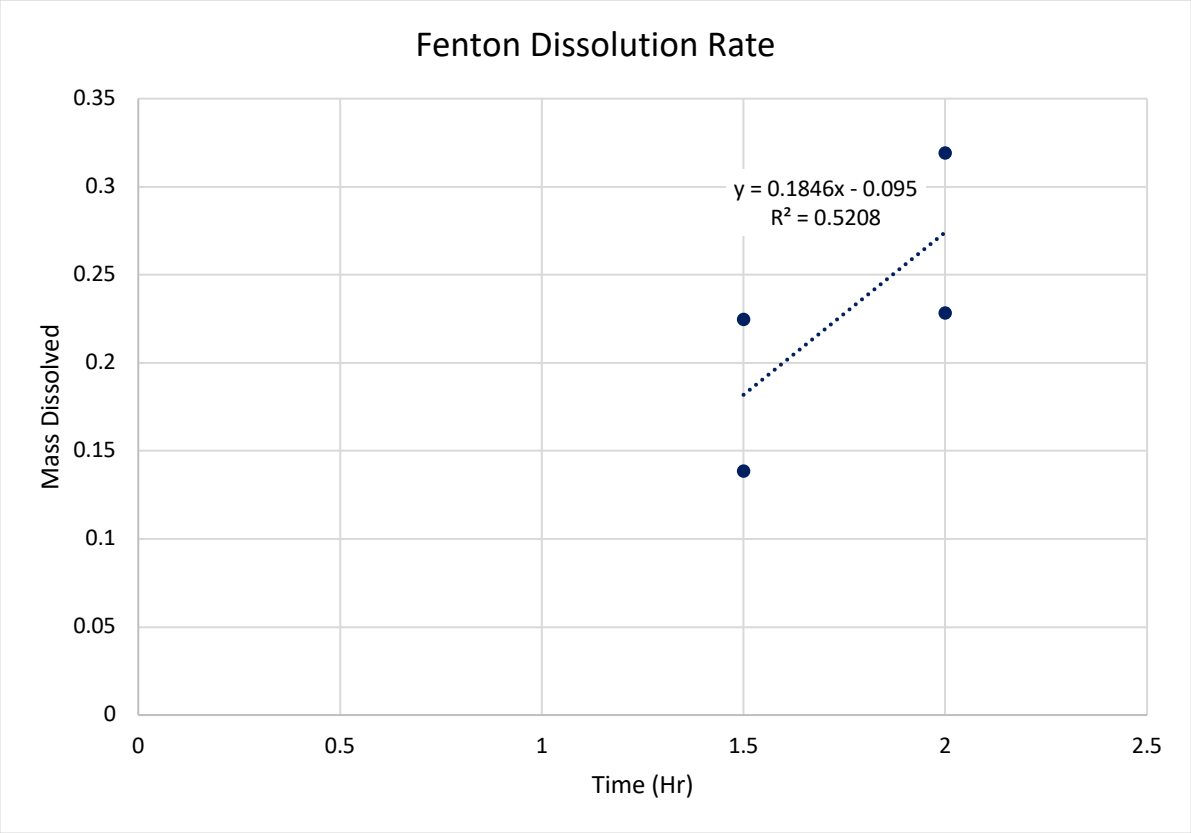

Fig. 7-1 Mass dissolved plotted over time for the Fenton reaction. Estimated 0.1846 g dissolved per hour, with offset for heating to reaction temperature.

Conclusion

In this section, the effects of modifying the hydrogen peroxide/ethanol solution to incorporate a Fenton reagent was investigated. It was determined that the temperature required for decomposition to occur was greatly reduced. It was also found that lower concentrations of hydrogen peroxide could also be used to decompose the epoxy. The conclusion is that use of the Fenton reaction could decrease the energy and chemical usage when compared to the original hydrogen peroxide/ethanol process, and thus could make an industrial scale of the process cheaper.

Chapter 8 Summary and Conclusion

Carbon fiber-reinforced composites are rapidly expanding into a variety of products used across many markets, ranging from aerospace to consumer products. Given their widespread use, high cost, and material design to resist mechanical failure it is important to develop an inexpensive, environmentally benign method to dissolve the epoxy and recover the fiber while maintaining their mechanical strength so that they can be reintroduced to the market at a reduced cost. Current recycling mechanisms being researched are unable to simultaneously meet all three criteria.

In this dissertation, a new solution of hydrogen peroxide and ethanol was investigated at elevated temperatures to dissolve epoxy and recover fibers from carbon fiber-reinforced epoxy composites. The effectiveness of this solution in fiber recovery and fiber strength retention was evaluated using scanning electron microscopy and electron dispersive spectroscopy. Fiber strength was measured using Instron tensile testing. A kinetic model was developed to predict time to complete fiber recovery and determine optimal reaction parameters to maximize fiber recovery. The fiber recovery rate and strength retention of this method was compared to the use of highly concentrated sulfuric acid. The hydrogen peroxide/ethanol solution was then modified to the Fenton reaction in order to reduce the required reaction temperature and chemical concentrations.

The results of this work found that usage of hydrogen and ethanol mixed together at elevated temperatures beginning at 120°C resulted in significant epoxy dissolution and carbon fiber recovery. Fiber strength was well preserved, with a tensile strength loss of 16% – 18%. No highly dangerous compounds were formed. The kinetic model was built using easily controlled variables and correlated well with experimental data. The solution developed was determined to be more effective compared to the use of highly concentrated sulfuric acid while maintaining

similar fiber strength. Finally, initial results of experiments utilizing the Fenton reagent found a significant reduction in temperature required for significant epoxy dissolution.

The conclusion of this work is that using hydrogen peroxide and ethanol together at elevated temperatures results in an effective, inexpensive dissolving solution that is inexpensive and ultimately benign. This solvolysis method results in recovered fibers that retain upwards of 80% of its strength and proves to be more effective than any other current method since it meets all desired criteria. Additionally, modification to a Fenton solution that adds ferrous ions and lowers the pH significantly reduces the required temperature for reaction, resulting in a process that would be even cheaper due to less energy used.

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